

Supplementary Information

**Preparation and nanoaggregate formation ability in water of
amphiphilic ladder-like polymers with parallelly linked hydrophilic
polyether and hydrophobic polysiloxane chains**

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Experimental section

Materials. Ethylene glycol dimethyl ether (purity: 99.0%) and potassium bromide (KBr, purity: 99.0%) were purchased from Nacalai Tesque, Inc. Allyl glycidyl ether (purity: ~99.0%), 3-mercaptopropyl dimethoxymethylsilane (MPDMMS, purity: ~95.0%), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO, purity: ~96.0%), dimethoxydimethylsilane (DMDMS, purity: ~98.0%), polyethylene glycol monomethyl ether acrylate (PEG-A; $n = ca. 13$, stabilized with hydroquinone monomethyl ether), tetramethylsilane (TMS, purity: ~99.0%), tris(2,4-pentanedionato)chromium(III) ($\text{Cr}(\text{acac})_3$, purity: ~98.0%) and tetraphenylporphyrin (TPP, purity: ~98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Potassium phenolate (purity: unknown), tetrahydrofuran (THF, purity: ~99.5%), *N,N*-dimethylformamide (DMF, purity: ~95.0%), diethyl ether (purity: ~99.5%), methanol (purity: ~99.5%), concentrated hydrochloric acid (conc. HCl, purity 35.0%–37.0%), dimethyl sulfoxide (DMSO, purity: ~99.0%), isopropyl alcohol (purity: ~99.7%), acetone (purity: ~99.0%), chloroform (purity: ~99.0%), ethyl acetate (purity: ~99.5%), hexane (purity: ~96.0%), methanol- d_4 (CD_3OD , purity: ~99.0%) and chloroform- d (CDCl_3 , purity: ~99.8%) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. Ethanol (purity: ~99.5%) was purchased from Japan Alcohol Trading Co., Ltd. PEG-*block*-PDMS-*block*-PEG (product code: DBE-C25) was purchased from Gelest Inc.

Preparation of poly(allyl glycidyl ether) (PAGE). PAGE was prepared according to a previous report.⁴⁷ Potassium phenolate (0.078 g, 0.67 mmol, calculated for 100% purity) was lyophilized for over 12 h, dissolved as an initiator in dried ethylene glycol dimethyl ether (15 mL) and repeatedly evacuated and purged with argon. While stirring, allyl glycidyl ether (2.536 g, 22.0 mmol) was added to the mixture. After stirring the reaction mixture at 110°C for 24 h under anhydrous conditions, it was poured into water (450 mL) and stirred at room temperature. The water-insoluble portion was then isolated by centrifugation, yielding PAGE as a light-brown viscous liquid (1.686 g, yield 67%, calculated according to the ideal chemical formula of the repeating unit of PAGE [$\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$), FW = 114.14]). The number-average molecular weight (M_n) of PAGE was estimated to be 2.5×10^3 by gel permeation chromatography (GPC; $M_w/M_n = 1.31$). Additionally, the average degree of polymerization was calculated to be 46 using the integral ratio of signal **e** to the signals **c**, which correspond to the phenolate-initiated end

groups and the double bonds in the repeating units, respectively, in the ^1H NMR spectrum in CD_3OD (Fig. S1). Considering the formula weights of the initiating units and repeating units, the ^1H NMR-based M_n was calculated to be 5.3×10^3 . ^1H NMR (400 MHz, CD_3OD , Fig. S1): δ 7.32–7.23 and δ 6.97–6.89 (m, 5H, PhO –), δ 6.06–5.98 (br, 1H, $-\text{OCH}=\text{CHCH}_3$), δ 5.98–5.81 (m, 1H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), δ 5.40–5.10 (m, 2H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), δ 4.42–4.29 (m, 1H, $-\text{OCH}=\text{CHCH}_3$), δ 4.10–3.93 (m, 2H, $-\text{OCH}_2\text{CH}=\text{CH}_2$), δ 3.81–3.41 (m, 10H, $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)\text{O}$ – and $-\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}=\text{CHCH}_3)\text{O}$ –), δ 1.61–1.49 (d, $J = 6.87$ Hz, 3H, $-\text{OCH}=\text{CHCH}_3$).

Preparation of PGE–PAMS (Scheme 1). A solution of PAGE (0.114 g, 1.0 mmol unit) in dehydrated THF (1 mL) and MPDMMS (0.285 g, 1.5 mmol) in dehydrated THF (1 mL) was added to BAPO (0.007 g, 15 μmol). The resulting mixture was stirred at room temperature under an argon atmosphere and then irradiated with light (wavelength: 380–420 nm) for 5 min. Subsequently, DMF (1000 mL) and purified water (360 μL , 20 mmol) were added to the solution, which was then stirred at 120°C for 120 h. The mixture was concentrated to *ca.* 10 mL using a rotary evaporator at *ca.* 80°C, poured into diethyl ether (300 mL) and stirred at room temperature. The diethyl ether-insoluble portion was isolated by decantation and washed with diethyl ether (~100 mL, three times). The isolated product was dissolved in methanol (2 mL), and the resulting solution was poured into diethyl ether (60 mL) and stirred at room temperature. The diethyl ether-insoluble portion was again isolated by decantation and washed with diethyl ether (~50 mL, three times). Finally, the product was dissolved in water (15 mL) and lyophilized, yielding PGE–PAMS as a light-brown viscous solid (0.423 g, yield 128%, calculated using the ideal chemical formula for the repeating unit of PGE–PAMS ($[\text{OC}_6\text{H}_5, \text{FW} = 93.10]/[\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_3\text{H}_6\text{SC}_3\text{H}_6)\text{SiO}(\text{CH}_3), \text{FW} = 234.39]/[\text{OCH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2), \text{FW} = 114.14]/[\text{SiO}(\text{CH}_3)(\text{C}_3\text{H}_6\text{SH}), \text{FW} = 134.27] = 0.02/0.78/0.07/0.13$). The yield exceeded 100% due to the high viscosity of the product, which prevented the complete removal of the solvent. ^1H NMR (400 MHz, CD_3OD , Fig. 2): δ 3.91–3.48 (br, 5H, $-\text{O}-\text{CH}_2\text{CH}(\text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2)-\text{O}$ –), δ 3.48–3.39 (br, residual methanol), δ 3.25–3.10 (br, 2H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2-$), δ 3.10–2.64 (br, 4H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 2.15–1.98 (br, 2H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2-$), δ 1.98–1.74 (br, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 1.05–0.54 (br, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 0.42–0.02 (br, 3H, CH_3Si –). FT-IR (KBr,

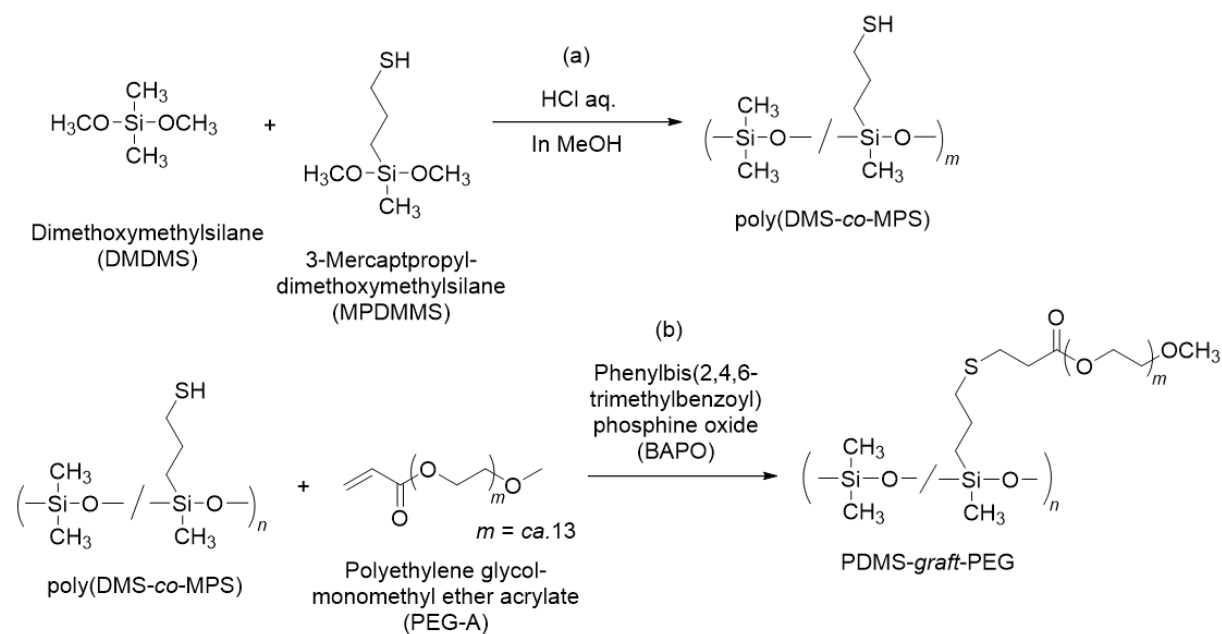
Fig. S2): 1124 cm^{-1} (siloxane bond and ether bond). ^{29}Si NMR (79.4 MHz, CH_3OD): δ -17.4–-21.2 (D^2), δ -21.2–-24.0 (D^2).

Preparation of poly(DMS-*co*-MPS) (Scheme S1a). As a precursor for PDMS-*graft*-PEG, poly(DMS-*co*-MPS) was prepared as follows: MPDMMMS (0.759 g, 4.0 mmol) and DMDMS (1.472 g, 12.0 mmol) were dissolved in methanol (1296 μL , 32 mmol), followed by the addition of water (2880 μL , 160 mmol) and conc. HCl (272 μL , 3.2 mmol). The mixture was stirred at room temperature for 30 min under an argon atmosphere and then heated at *ca.* 70°C in an open system until the solvent completely evaporated (*ca.* 12 h). Subsequently, 2.5 mL methanol was added at room temperature, and the methanol-insoluble portion was isolated by decantation and washed with methanol (six times). Finally, the product was dried under reduced pressure, yielding poly(DMS-*co*-MPS) as a colorless, transparent liquid (0.147 g, yield 10%, calculated using the ideal chemical formula of the repeating unit of poly(DMS-*co*-MPS) ($[\text{SiO}(\text{CH}_3)_2]$, FW = 74.15)/ $[\text{SiO}(\text{CH}_3)(\text{C}_3\text{H}_6\text{SH})]$, FW = 134.27] = 0.74/0.26). ^1H NMR (400 MHz, CDCl_3 , Fig. S3): δ 2.59–2.47 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 1.71–1.60 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 1.38–1.27 (br, 1H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 0.71–0.57 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 0.15–0.05 (s, 9H, $-\text{SiCH}_3$). GPC: $M_n = 7.76 \times 10^3$, $M_w/M_n = 1.17$. ^{29}Si NMR (79.4 MHz, CDCl_3 , Fig. S4): δ -10.3–-11.2 ($\text{D}^1_{(\text{DM})}$), δ -12.1–-12.9 ($\text{D}^1_{(\text{SH})}$), δ -21.0–-22.5 ($\text{D}^2_{(\text{DM})}$), δ -22.5–-23.7 ($\text{D}^2_{(\text{SH})}$).

Preparation of PDMS-*graft*-PEG (Scheme S1b). A solution of poly(DMS-*co*-MPS) (0.047 g, 0.52 mmol unit) in dehydrated THF (0.5 mL) and PEG-A (0.079 g, 0.12 mmol) in dehydrated THF (0.5 mL) was added to BAPO (0.001 g, 1.2 μmol). The resulting solution was stirred at room temperature under an argon atmosphere and then irradiated with light (wavelength: 380–420 nm) for 5 min. Finally, THF was removed using a rotary evaporator, and the product was dried under reduced pressure, yielding PDMS-*graft*-PEG as a colorless, transparent liquid (0.1047 g, yield 77%, calculated using the ideal chemical formula of the repeating unit of PDMS-*graft*-PEG ($[\text{SiO}(\text{CH}_3)_2]$, FW = 74.15)/ $[\text{SiO}(\text{CH}_3)(\text{C}_3\text{H}_6\text{SC}_2\text{H}_4\text{CO}(\text{OC}_2\text{H}_4)_{13}\text{OCH}_3)]$, FW = 793.05] = 0.74/0.26). ^1H NMR (400 MHz, CDCl_3 , Fig. S5): δ 4.33–4.16 (broad, 2H, $-\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2-$), δ 3.77–3.56 (m, 54H, $-\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_{12}\text{OCH}_3$), δ 3.42–3.35 (s, 3H, $-\text{C}(=\text{O})\text{OCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_{12}\text{OCH}_3$), δ 2.82–2.72 (m, 2H, $-\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2-$), δ

2.72–2.59 (m, 2H, $-\text{SCH}_2\text{CH}_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2-$), δ 2.59–2.46 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), δ 1.74–1.54 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), δ 1.40–1.23 (br, 1H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$), δ 0.72–0.54 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-$), δ 0.20–0.02 (s, 9H, $-\text{SiCH}_3$). GPC: $M_n = 1.71 \times 10^4$, $M_w/M_n = 1.18$.

Measurements. FT-IR spectra were recorded using an FT/IR-4200 spectrometer (JASCO Corporation, Tokyo, Japan). ^1H and ^{29}Si NMR spectra were recorded with an ECX-400 spectrometer (JEOL RESONANCE Inc., Tokyo, Japan). The average molecular weight and molecular weight distribution were determined by GPC using poly(methyl methacrylate) standards. For the GPC analysis, SHIMADZU CTO-20AC and a SHIMADZU RID-20A (Shimadzu Corporation, Kyoto, Japan) were employed, using Shodex KF-803L (bead size: 6 μm , measurable molecular weight range: 1.0×10^2 – 7.0×10^4) and Shodex KF-805L (bead size: 6 μm , measurable molecular weight range: 1.0×10^2 – 5.0×10^6) columns. THF was used as the eluent and pumped through the system at a flow rate of 1.0 mL min^{-1} at 40°C. Transmission electron microscopy (TEM) measurements were performed using a JEM-2100 plus transmission electron microscope equipped with a LaB_6 source (JEOL Ltd., Tokyo, Japan) and operated at an acceleration voltage of 200 kV. TEM images were then recorded with a $3,072 \times 3,072$ pixel Rio 9 CMOS camera (Gatan Co., Ltd., USA). A 1.0 wt% aqueous solution of PGE–PAMS was prepared, and 10 μL of the solution was dropped onto an elastic carbon grid (Okenshoji Co., Ltd.), left to stand for 30 s, and then absorbed with filter paper and dried. Particle sizes were measured using an ELSZ-2000 DLS apparatus (Otsuka Electronics Co., Ltd., Osaka, Japan). To this aim, PGE–PAMS was dissolved in water, DMSO, methanol, ethanol and isopropyl alcohol at 0.1 w/v% and left to stand overnight. The resulting solution (3.0 mL) was then placed in a quartz cell (GL Science Inc., Tokyo, Japan) for DLS measurements. Volume-average distributions were calculated using the cumulant method. The refractive indices of the solvents used in the measurements were 1.3300 for water, 1.4780 for DMSO, 1.3299 for methanol, 1.3628 for ethanol and 1.3781 for isopropyl alcohol. The UV–Vis spectra were recorded using a JASCO V-630 spectrophotometer (JASCO Corporation, Tokyo, Japan). In the measurements shown in Fig. 8, the heating and cooling processes were controlled using a Peltier ETCR-762 thermosted cell holder and CTU-100 circulating water sources (JASCO Corporation, Tokyo, Japan), with temperatures ranging from 5°C to 90°C at a rate of 1°C min^{-1} . The transmittance ($\lambda = 500$ nm) of the 0.1 w/v% aqueous solution was measured during heating from 5°C to 90°C under a nitrogen atmosphere.



Scheme S1 Preparation of (a) poly(DMS-co-MPS) and (b) PDMS-graft-PEG.

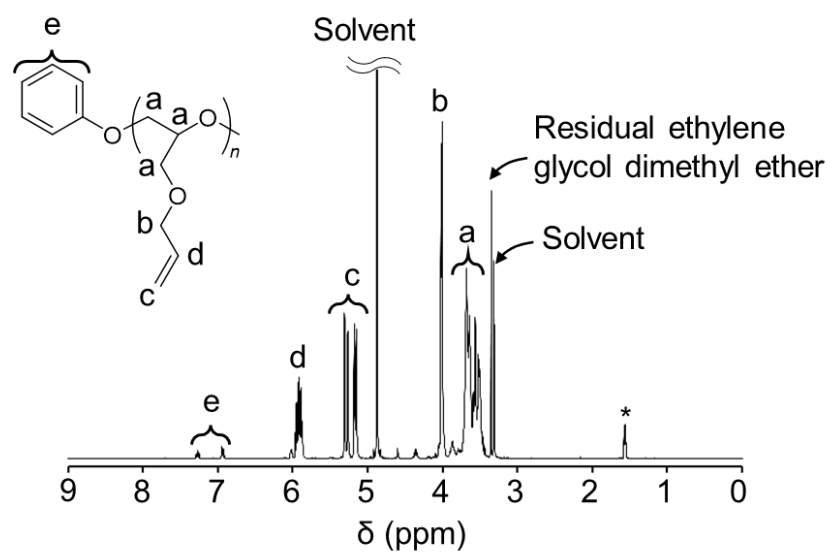


Fig. S1 ^1H NMR spectrum of PAGE in CD_3OD . The chemical shifts are referenced to CD_3OD (δ 3.31). *: Unknown signal.

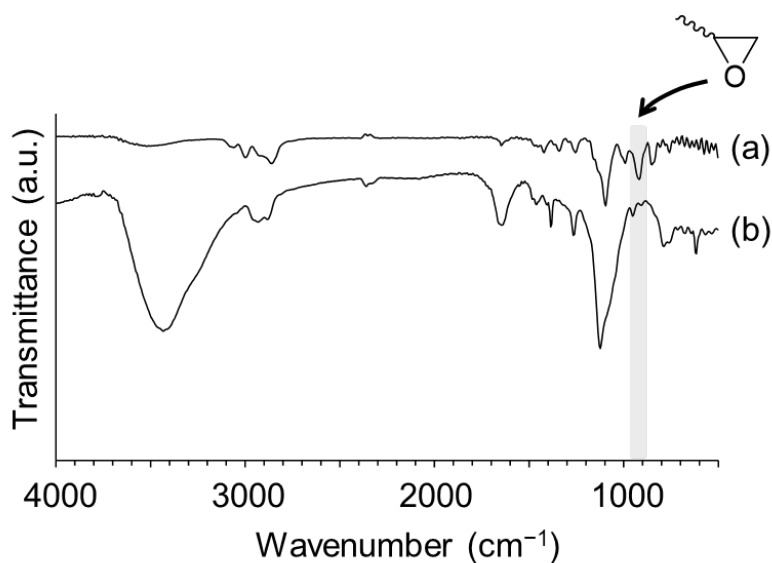


Fig. S2 FT-IR spectra of (a) allyl glycidyl ether and (b) PGE-PAMS in KBr pellets.

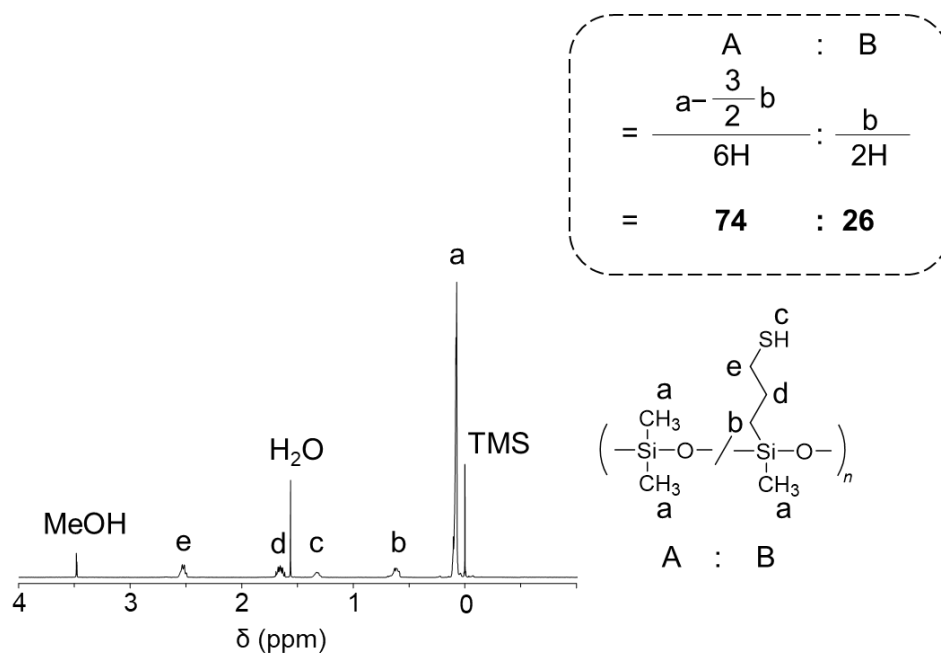


Fig. S3 ^1H NMR spectrum of poly(DMS-*co*-MPS) in CDCl_3 . The chemical shifts are referenced to TMS (δ 0.0).

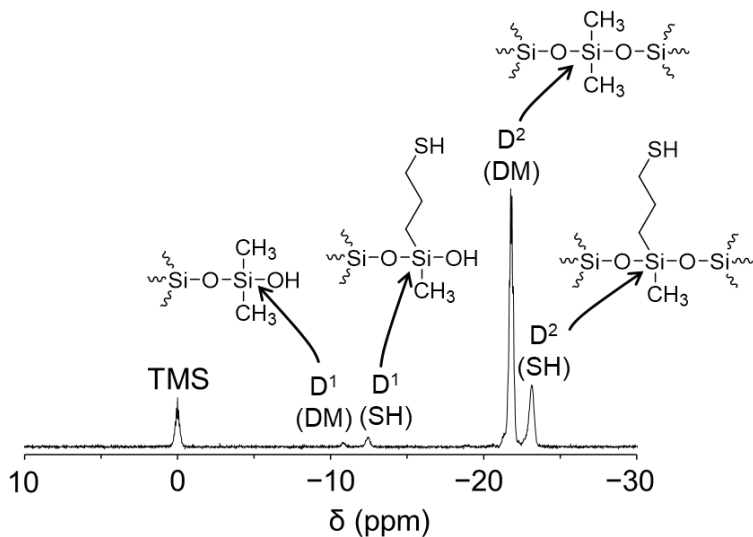


Fig. S4 ^{29}Si NMR spectrum of poly(DMS-*co*-MPS) in CDCl_3 at room temperature. A small amount of $\text{Cr}(\text{acac})_3$ was added as a relaxation agent. The chemical shifts are referenced to TMS (δ 0.0).

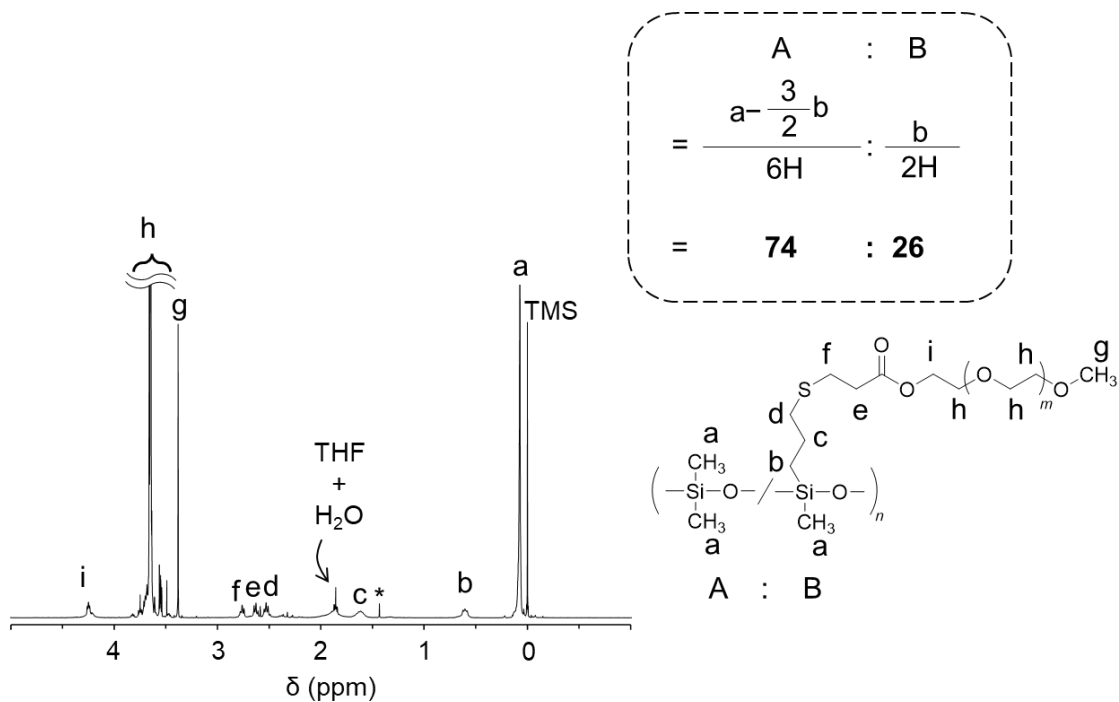


Fig. S5 ^1H NMR spectrum of PDMS-*graft*-PEG in CDCl_3 . The chemical shifts are referenced to TMS (δ 0.0). *: Unknown signal.

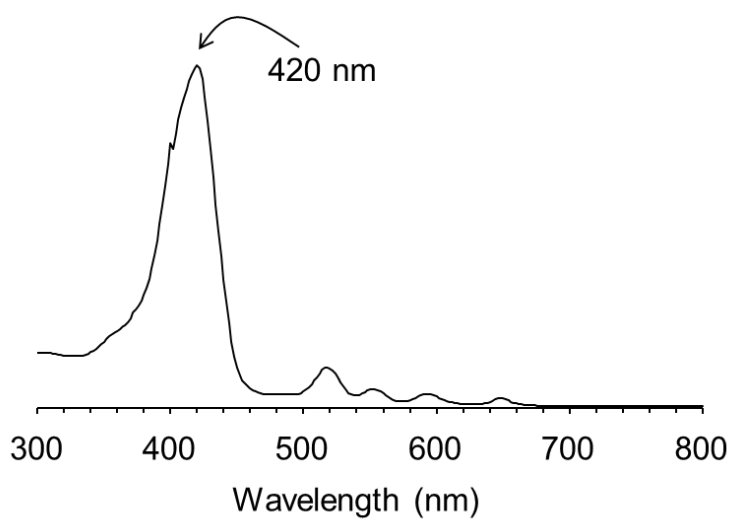


Fig. S6 UV-Vis spectrum of a water/DMF (9/1, v/v) solution of a mixture of PGE-PAMS (2.0×10^{-3} w/v%) and TPP (5.0×10^{-4} w/v%).

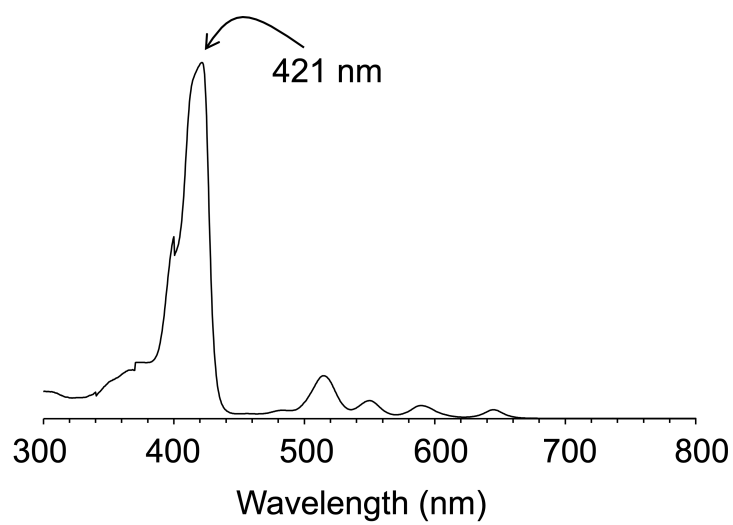


Fig. S7 UV-Vis spectrum of a chloroform solution of TPP (5.0×10^{-4} w/v%).

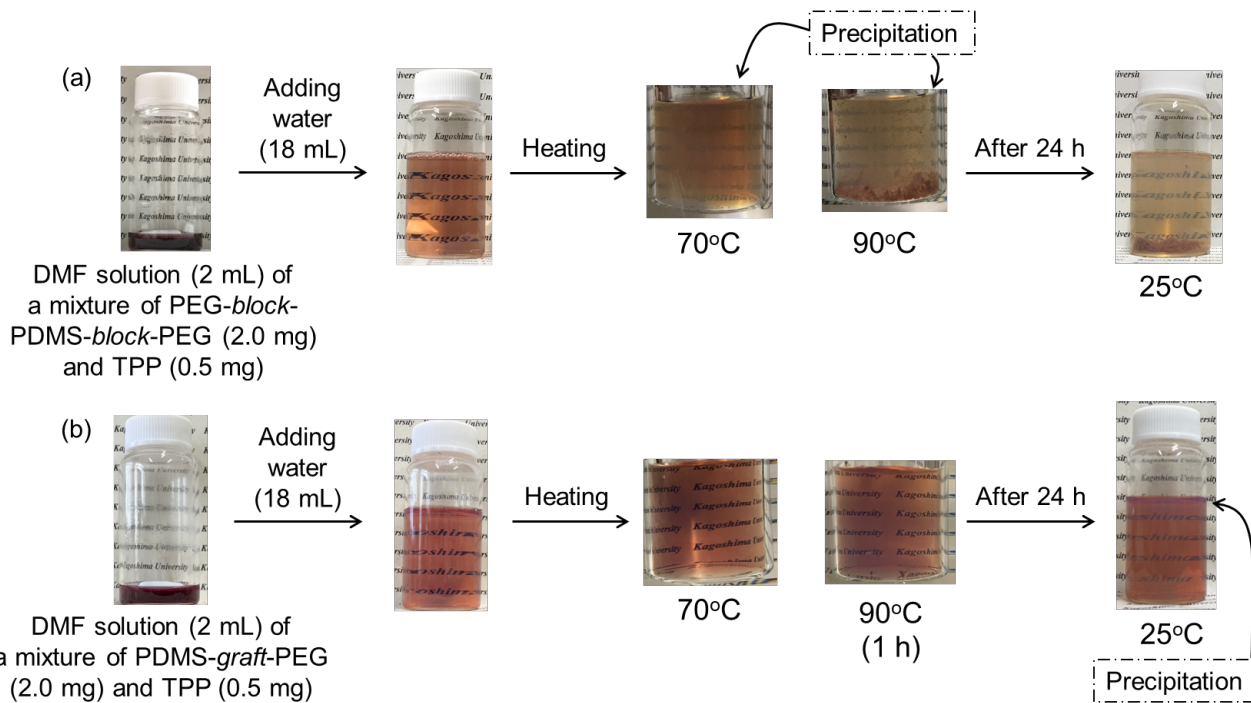


Fig. S8 Photographs of water/DMF (9/1, v/v) solutions of (a) a mixture of PEG-*block*-PDMS-*block*-PEG and TPP and (b) a mixture of PDMS-*graft*-PEG and TPP at varying temperatures.