Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Thermoresponsive Properties of 3-, 4-, 6-, and 12-Armed Star-Shaped Poly[2-(dimethylamino)ethyl methacrylate]s Prepared by Core-First Group Transfer Polymerization

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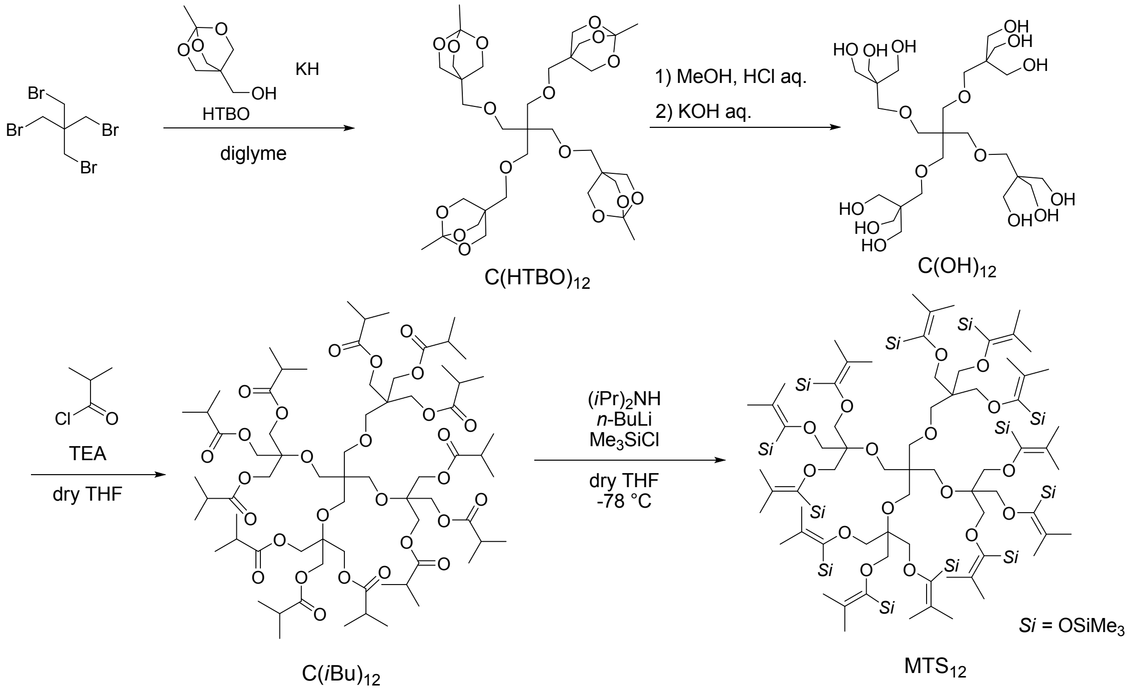
Scheme S1. Synthetic route of MTS$_{12}$



Synthesis of (1-Methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methanol (HTBO).[1] In a three-neck flask, pentaerythritol (50.0 g, 0.367 mol) and *p*-toluenesulfonic acid·H_2O (1.29 g, 6.77 mmol) were dissolved in dry toluene (400 mL) and the mixture was refluxed. Triethyl orthoacetate (80.8 mL, 0.44 mol) was then added. After the whole mixture was continuously refluxed for 48 h, a small amount of triethylamine was added to stop the reaction, and the solvent was removed under reduced pressure. The residue was recrystallized in toluene to give a white solid product. Yield, 46.8 g (80%).

Synthesis of Tetrakis{[(1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methyl]oxymethyl} methane (C(HTBO)$_4$).[2] In a three-neck flask equipped with a reflux condenser, a magnetic stirrer, and an dropping funnel, potassium hydride (1.48 g, 26.4 mmol) and diglyme (40 mL) were added under an argon atmosphere. A solution of (1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)- methanol (3.39 g, 21.1 mmol) in diglyme (30 mL) was added dropwise at 0 °C, and the mixture was stirred for 3 h. A solution of pentaerythritol tetrabromide (1.86 g, 4.81 mmol) in diglyme (40 mL) was added dropwise. After the mixture was further refluxed for 12 h, a small amount of distilled water was added to stop the reaction. The mixture was then poured in ice water, and the precipitate is filtered, washed with water. The obtained solid was then recrystallized in acetonitrile/toluene (v/v = 4/1) mixed solvent to give a white product. Yield, 1.28 g (38%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.45 (s, 12H, $C\mathit{H}_3C$-), 3.12 (s, 8H, $C(C\mathit{H}_2OCH_2C$-$)_4$), 3.21 (s, 8H, $C(CH_2OC\mathit{H}_2C$-$)_4$), 3.96 (s, 24H, $CH_3C(C\mathit{H}_2O$-$)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 23.1 (4C, $\mathit{C}H_3C(OCH_2)_3CCH_2$-), 35.0 (4C, $CH_3C(OCH_2)_3\mathit{C}CH_2$-), 45.8 (1C, $\mathit{C}(CH_2OC\mathit{H}_2C$-$)_4$), 69.1 (12C, $CH_3C(O\mathit{C}H_2)_3CCH_2$-), 69.9 (4C, $CH_3C(OCH_2)_3C\mathit{C}H_2$-), 70.2 (4C, $C(\mathit{C}H_2OC\mathit{H}_2C$-$)_4$), 108.7 (4C, $CH_3\mathit{C}$-).

Synthesis of Tetrakis{2,2,2-tris[(hydroxy)methyl]ethyloxymethyl}methane ($C(OH)_{12}$).[2] In a 100 mL flask, tetrakis{[(1-methyl-2,6,7-trioxabicyclo[2.2.2]octan-4-yl)methyl]oxymethyl}methane (2.0 g, 2.8 mmol), methanol (30 mL), and HCl aq. (0.2 mL, 1.0 mol L^{-1}) were sequentially added, and the mixture was stirred under r.t. for 3 h. A KOH aq. (1.0 mL, 10.0 mmol L^{-1}) was dropped into the mixture. The obtained white solid was filtered and dried to give the $C(OH)_{12}$. Yield, 1.20 g (70 %). ^{1}H NMR (400 MHz, D_2O, δ): 3.40-3.50 (d, J = 4.6 Hz, 16H, $C(C\mathit{H}_2OC\mathit{H}_2C\text{-})_4$), 3.12 (s, 24H, $\text{-}C\mathit{H}_2OH$).

Synthesis of Tetrakis{2,2,2-tris[(isobutyryloxy)methyl]ethyloxymethyl}methane ($C(\mathit{i}Bu)_{12}$). To a mixture of $C(OH)_{12}$ (3.65 g, 6.00 mmol) and triethylamine (15 mL, 101 mmol) in dry THF (200 mL), isobutyryl chloride (9.2 mL, 86 mmol) in THF (50 mL) was slowly added at 0 °C under a nitrogen atmosphere. After the reaction mixture was stirred at r.t. for 42 h, the resulting salt was removed by filtration and the filtered organic layer was washed with saturated aqueous $NaHCO_3$, aqueous NaCl, and distilled water. The organic layer was dried over anhydrous Na_2SO_4 and then evaporated to remove the solvent. The crude product was purified by column chromatography (Al_2O_3 gel, dichloromethane) to give $C(\mathit{i}Bu)_{12}$ as a colorless liquid. Yield, 5.30 g (61 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.16 (d, J = 6.8 Hz, 72H, $(C\mathit{H}_3)_2CH\text{-}$), 2.57 (m, 12H, $(CH_3)_2C\mathit{H}\text{-}$), 3.33 (s, 8H, $C(C\mathit{H}_2OCH_2C(CH_2OCOCH(CH_3)_2)_3)_4$), 3.39 (s, 8H, $C(CH_2OC\mathit{H}_2C(CH_2OCOCH\text{-}(CH_3)_2)_3)_4$), 4.10 (s, 24H, $\text{-}C\mathit{H}_2OCO\text{-}$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 19.1 (24C, $(\mathit{C}H_3)_2CH\text{-}$), 34.1 (12C, $(CH_3)_2\mathit{C}H\text{-}$), 43.2 (4C, $C(CH_2OCH_2\mathit{C}(CH_2OCOCH(CH_3)_2)_3)_4$), 45.8 (4C, $\mathit{C}(CH_2OCH_2C(CH_2OCOCH(CH_3)_2)_3)_4$), 62.9 (12C, $C(CH_2OCH_2C(\mathit{C}H_2OCOCH(CH_3)_2)_3)_4$), 70.2 (12C, $C(CH_2O\mathit{C}H_2C(CH_2OCOCH(CH_3)_2)_3)_4$), 71.0 (12C, $C(\mathit{C}H_2OCH_2C(CH_2OCOCH(CH_3)_2)_3)_4$), 176.6 (12C, $\mathit{C}{=}O$).

Synthesis of Tetrakis{2,2,2-tris[(2-methyl-1-(trimethylsilyloxy)prop-1-enyloxy)methyl]ethyloxy-methyl}methane (MTS_{12}). To a solution of diisopropylamine (4.10 mL, 29.9 mmol) in dry THF (ca. 40 mL) in a 100-mL cock-attached flask, *n*-butyllithium (18.4 mL, 29.9 mmol; 1.62 mol L^{-1} in *n*-hexane) was added dropwise at 0 °C under an argon atmosphere. After stirring for 1 h, $C(\mathit{i}Bu)_{12}$ (3.25 g, 2.24 mmol) in dry THF was slowly added. The reaction mixture was stirred at −78 °C for 1 h, and then chlorotrimethylsilane (9.40 mL, 64.5 mmol) was slowly added. After the entire reaction mixture was stirred at r.t. for 15 h, impurities with lower boiling temperatures were removed under reduced pressure (140 °C, 0.04 mmHg). The residue was then dissolved in dry *n*-hexane and filtered to remove the salt through a 0.45 μm PTFE filter under an argon atmosphere in a glove box. *n*-Hexane was removed under reduced pressure (0.02 mmHg) at room temperature to give MTS_{12} as a yellow liquid. Yield, 4.91 g (95 %). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.18 (s, 108H, $(C\mathit{H}_3)_3Si\text{-}$), 1.48 (s, 36H, $(C\mathit{H}_3)_2C\text{-}$), 1.54 (s, 36H, $(C\mathit{H}_3)_2C\text{-}$), 3.39 (s, 8H, $C(C\mathit{H}_2OCH_2C(CH_2OOSi(CH_3)_3\text{-}C{=}C(CH_3)_2)_3)_4$), 3.48 (s, 8H, $C(CH_2OC\mathit{H}_2C\text{-})_4$), 3.79 (s, 12H, $\text{-}C\mathit{H}_2O(CH_3)_3SiOC{=}C(CH_3)_2)_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 0.4 (36C, $(\mathit{C}H_3)_3Si\text{-}$), 16.7 (s, 6C, $(\mathit{C}H_3)_2C{=}C$), 17.4 (d, 6C, $(\mathit{C}H_3)_2C{=}C$), 45.1 (4C, $C(CH_2OCH_2\mathit{C}\text{-})_4$), 46.1 (1C, $\mathit{C}(CH_2OCH_2C\text{-})_4$), 68.0 (12C, $\text{-}\mathit{C}H_2OOSi(CH_3)_3C{=}C(CH_3)_2$), 70.5 (4C, $C(CH_2O\mathit{C}H_2C(CH_2OOSi(CH_3)_3C{=}(CH_3)_2)_3)_4$), 70.6 (4C, $C(\mathit{C}H_2OCH_2C\text{-})_4$), 89.8 (12C, $(CH_3)_2\mathit{C}{=}$)), 148.7 (6C, $(CH_3)_3SiO\mathit{C}{=}C(CH_3)_2$)).

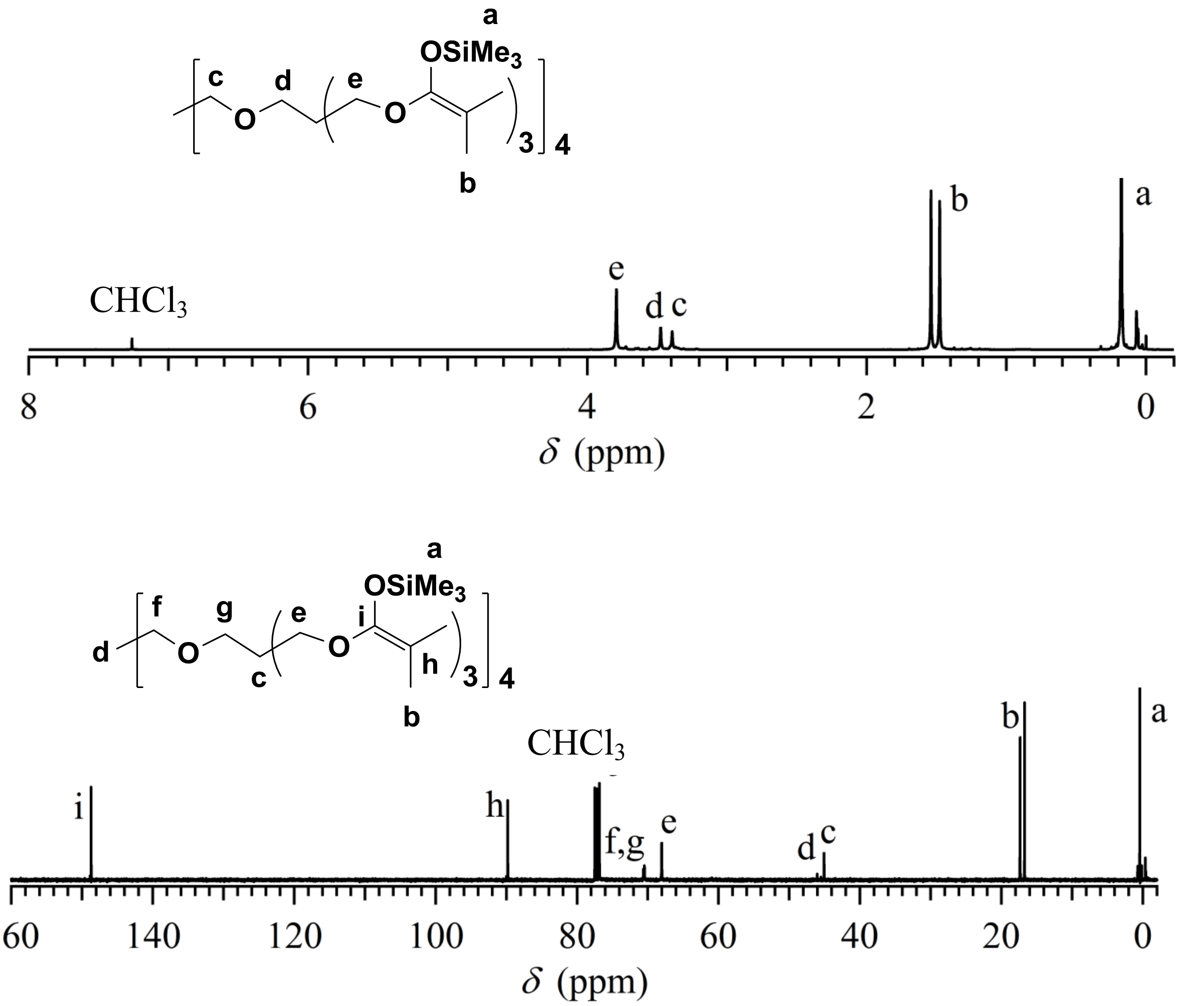


Figure S1. ^{1}H (upper) and ^{13}C (lower) NMR spectra of MTS_{12} in $CDCl_3$.

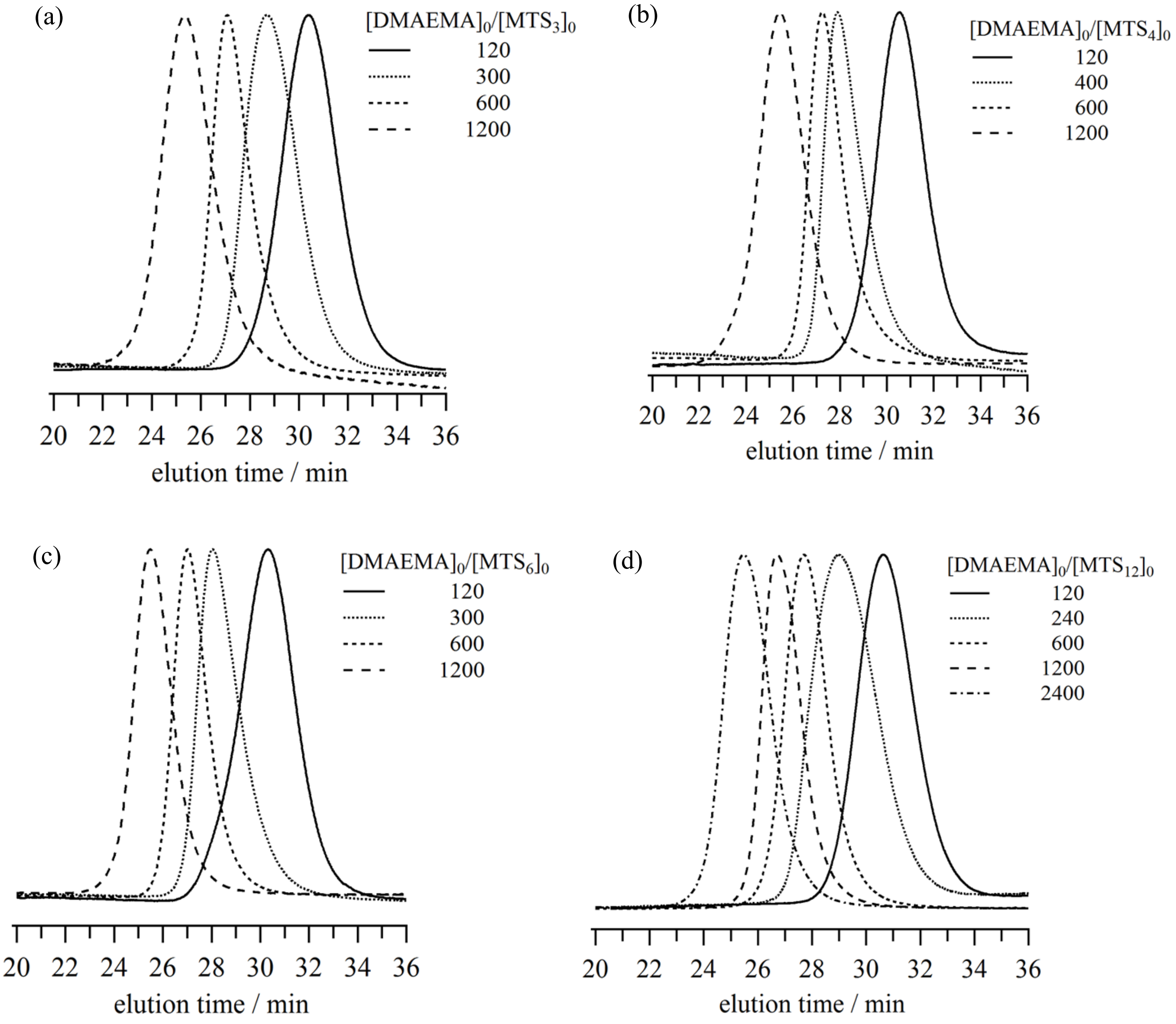


Figure S2. SEC traces of (a) *s*-PDMAEMA$_3$s, (b) *s*-PDMAEMA$_4$s, (c) *s*-PDMAEMA$_6$s, and (d) *s*-PDMAEMA$_{12}$s measured by SEC equipped with a RI detector in DMF containing 0.01 mol L^{-1} LiCl.

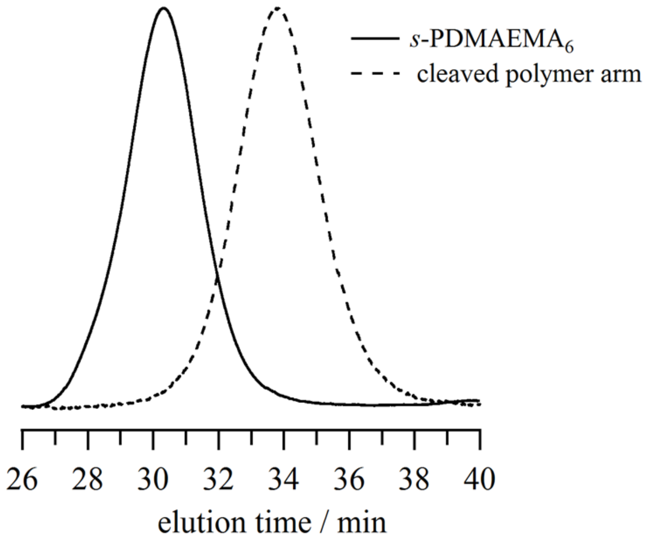


Figure S3. SEC traces of the parent six-armed *s*-PDMAEMA (solid line, $M_w/M_n = 1.20$) and the cleaved linear PDMAEMA arm (dashed line, $M_w/M_n = 1.13$) measured by SEC equipped with a RI detector in DMF containing 0.01 mol L^{-1} LiCl.

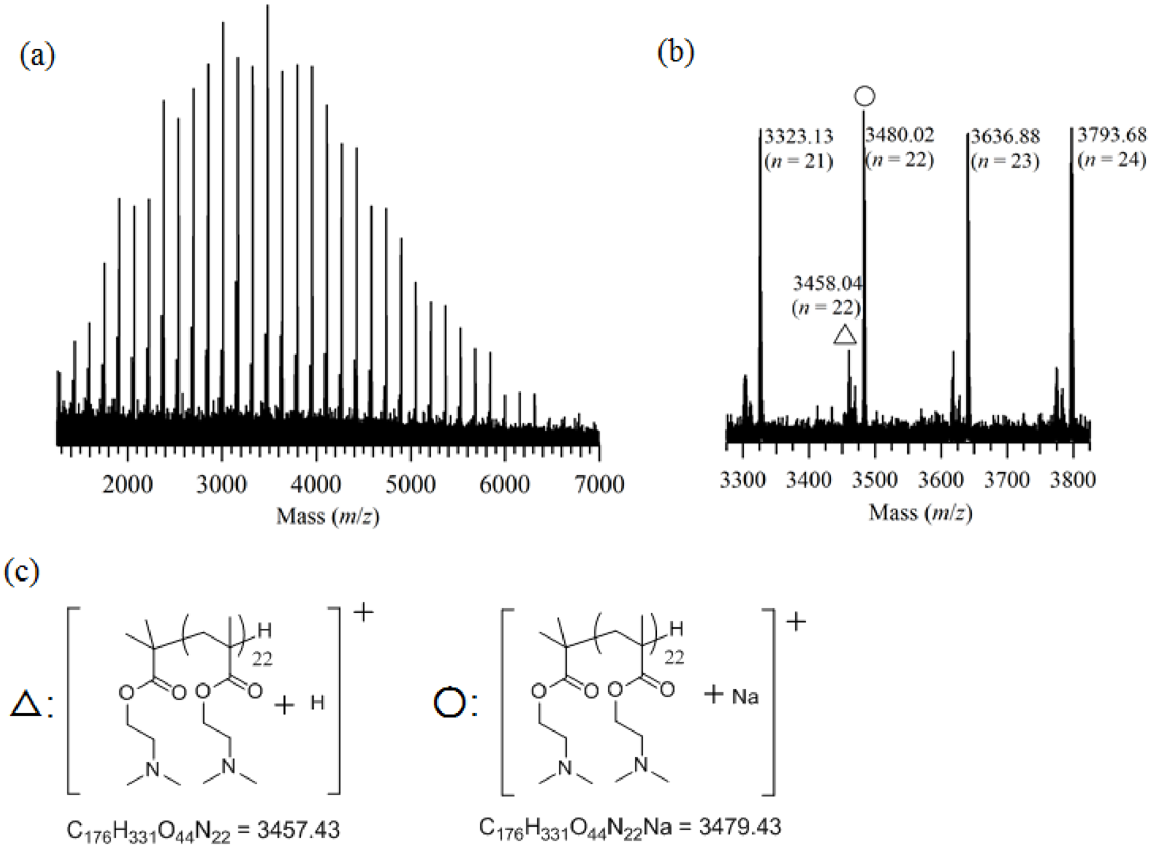


Figure S4. (a) MALDI-TOF MS spectrum (reflector mode) of the cleaved PDMAEMA, (b) expanded spectrum ranging from 3300 to 3800 Da, (c) predicted structures.

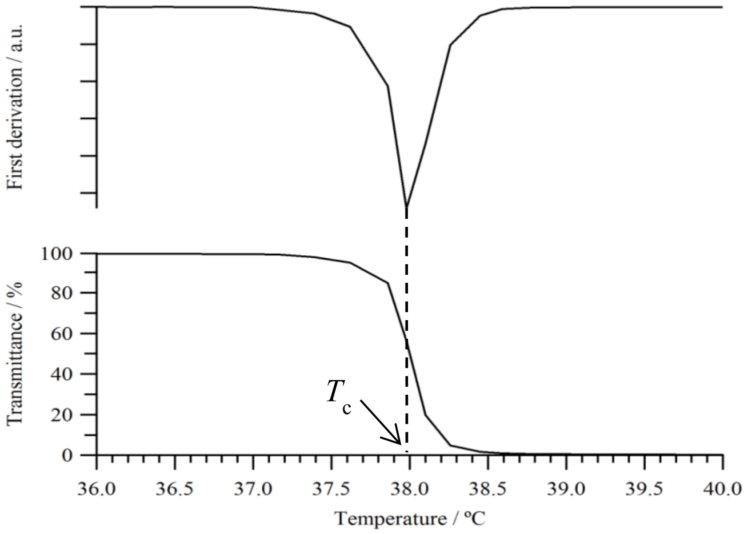


Figure S5. T_c determined by the derivation of the transmittance curve.

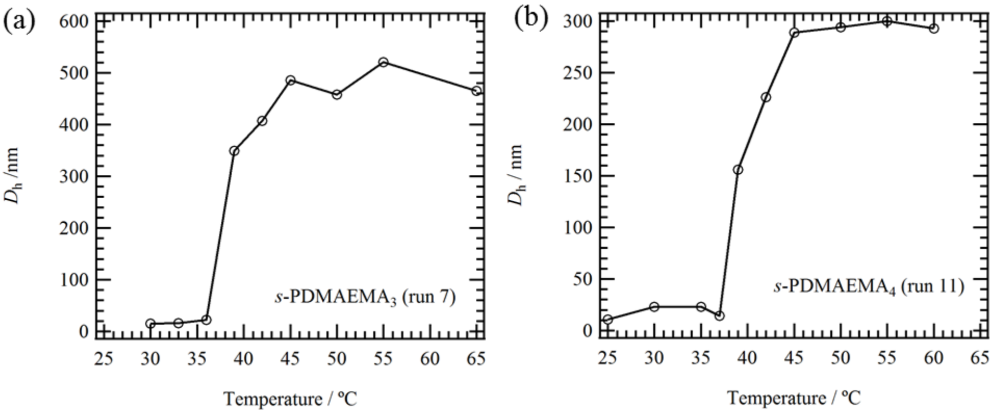


Figure S6. Hydrodynamic diameter dependence of (a) s-PDMAEMA$_3$ (run 7; $M_{w,MALS}$, 106 kg mol^{-1}) and (b) s-PDMAEMA$_4$ (run 11; $M_{w,MALS}$, 128 kg mol^{-1}) on temperature.

Reference

1. Yokoyama, Y.; Padias, A. B.; Bratoeff, E. A.; Hall, H. K., Jr. Macromolecules 1982, **15**, 11-17.

2. Padias, A. B.; Hall, H. K., Jr.; Tomalia, D. A.; McConnell, J. R. *J. Org. Chem.*, 1987, **52**, 5305-5312.