

Electronic Supplementary Information (ESI)

Multi-responsive (diethylene glycol) methyl ether methacrylate (DEGMA)-based copolymer systems.

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Polymer synthesis.

Synthesis of P(DEGMA-*stat*-MAA) (1)

DEGMA (8.68 g, 46.14 mmol), MAA (1.32 g, 15.36 mmol), 4-CPDB (0.1376 g, 0.49 mmol) and VAZO-88 (24.30 mg, 99.45 μ mol) were added to a Schlenk flask and DMF (16.10 mL, 60 wt. %) was added. The vessel was degassed using three freeze-pump-thaw cycles, before the flask was immersed in a temperature controlled oil bath set to 90 °C for 4 h. After cooling the reaction mixture, the polymer was isolated *via* precipitation into cold *n*-pentane three times. **1** was dried under high vacuum to remove residual solvent. 67% conversion. DP_{NMR} : 77. $M_1:M_2$: 61:16 (DEGMA:MAA). GPC: M_n 11 800, M_w 13 100, D 1.11.

Synthesis of P(DEGMA-*stat*-DMAEMA) (2)

DEGMA (7.82 g, 41.56 mmol), DMAEMA (2.18 g, 13.85 mmol), 4-CPDB (0.12 g, 0.44 mmol) and VAZO-88 (21.50 mg, 87.99 μ mol) were added to a Schlenk flask and DMF (16.12 mL, 60 wt. %) was added. The vessel was degassed using three freeze-pump-thaw cycles, before the flask was immersed in a temperature controlled oil bath set to 90 °C for 6 h. After cooling the reaction mixture, the polymer was isolated *via* precipitation into cold *n*-pentane three times. **2** was dried under high vacuum to remove residual solvent. 61% conversion. DP_{NMR} : 96. $M_1:M_2$: 71:25 (DEGMA:DMAEMA). GPC: M_n 21 200, M_w 26 000, D 1.23.

Synthesis of P (DEGMA) macroRAFT-CTA (3)

DEGMA (20.02 g, 0.11 mol), 4-CPDB (0.30 g, 1.06 mmol) and VAZO-88 (52.20 mg, 0.21 mmol) were added to a Schlenk flask and DMF (86.86 mL, 80 wt. %) was added. The vessel was degassed using three freeze-pump-thaw cycles, before the flask was immersed in a temperature controlled oil bath set to 90 °C for 4 h. After cooling the reaction mixture, the polymer was isolated *via* precipitation into cold *n*-pentane three times. **3** was dried under high vacuum to remove residual solvent. 57% conversion. DP_{NMR} : 67. GPC: M_n 10 900, M_w 12 000, D 1.10.

Synthesis of P(DEGMA-*b*-MAA) (4)

Polymer **3** (2.09 g, 0.16 mmol), MAA (0.63 g, 7.35 mmol), and VAZO-88 (7.19 mg, 29.43 μ mol) were added to a Schlenk flask and DMF (4.87 mL, 63 wt. %) was added. The vessel was degassed using three freeze-pump-thaw cycles, before the flask was immersed in a temperature controlled oil bath set to 90 °C for 4 h. After cooling the reaction mixture, the polymers were isolated *via* precipitation into cold *n*-pentane three times. The polymers were dried under high vacuum to remove residual solvent. 73% conversion. Total DP_{NMR}: 95. M₁:M₂: 67:28 (DEGMA:MAA). GPC: M_n 11 300, M_w 13 200, Đ 1.16.

Synthesis of P(DEGMA-*b*-DMAEMA) (5)

Polymer **3** (1.67 g, 0.12 mmol), DMAEMA (0.92 g, 5.87 mmol) and VAZO-88 (5.74 mg, 23.49 μ mol) were added to a Schlenk flask and DMF (5.12 mL, 65 wt. %) was added. The vessel was degassed using three freeze-pump-thaw cycles, before the flask was immersed in a temperature controlled oil bath set to 90 °C for 6 h. After cooling the reaction mixture, the polymers were isolated *via* precipitation into cold *n*-pentane three times. The polymers were dried under high vacuum to remove residual solvent. 91% conversion. Total DP_{NMR}: 104. M₁:M₂: 67:37 (DEGMA:DMAEMA). GPC: M_n 17 100, M_w 20 500, Đ 1.20.

In situ ¹H NMR – general information

Due to the heating limitations of the cryoprobe used for the ¹H NMR experiments, the *in situ* polymerisations were conducted at 75 °C and thus a lower temperature initiator (AIBN) was used. Any effects arising from the difference in half-life of the initiator were expected to be minimal. All other reaction conditions were kept the same. Since these reaction conditions varied slightly from the batch polymerisation conditions (90 °C; VAZO-88), the resulting polymers will be referred to as **1*** and **2*** in the below sections. The main implications are that the reactivity ratios calculated below will be slightly different to the monomer interplay that actually occurred during the batch polymerisations that produced polymers **1** and **2**. It should be noted however, that this difference is minor, since activation energies for radical propagation are relatively small for these sets of monomers.¹ Furthermore, as the reactivity ratios described in the below section were calculated from a single reaction with only one monomer feed ratio, the values obtained are merely rough estimates.

In situ ¹H NMR synthesis of P(DEGMA-*stat*-MAA) (**1***).

DEGMA (1.13 g, 6.04 mmol), MAA (0.17 g, 2.02 mmol), 4-CPDB (18.0 mg, 64.43 μ mol) and AIBN (2.1 mg, 12.79 μ mol) were mixed in a 2 mL vial to form a stock solution. A portion of the stock solution (0.25 g) was then mixed with DMF-*d*7 (0.53 g; 68 wt. %), and this solution was transferred to a gas-tight Schlenk NMR tube. The vessel was degassed using three freeze-pump-thaw cycles, before the sample was loaded into the NMR spectrophotometer. A ¹H spectra was obtained at 298 K (25 °C) before the

sample was removed and the cryoprobe heated to 348 K (75 °C). The sample was reloaded into the spectrophotometer, and spectra were recorded at 30 minute intervals over the course of 24 h. Serial processing of the ¹H spectra was done using the TopSpin software.

***In situ* ¹H NMR synthesis of P(DEGMA-*stat*-DMAEMA) (2*).**

DEGMA (2.37 g, 12.57 mmol), DMAEMA (0.66 g, 4.19 mmol), 4-CPDB (37.1 mg, 0.13 mmol) and AIBN (4.4 mg, 26.80 μmol) were mixed in a 2 mL vial to form a stock solution. A portion of the stock solution (0.27 g) was then mixed with DMF-*d*7 (0.49 g; 65 wt. %), and this solution was transferred to a gas-tight Schlenk NMR tube. The vessel was degassed using three freeze-pump-thaw cycles, before the sample was loaded into the NMR spectrophotometer. A ¹H spectra was obtained at 298 K (25 °C) before the sample was removed and the cryoprobe heated to 348 K (75 °C). The sample was reloaded into the spectrophotometer, and spectra were recorded at 30 minute intervals over the course of 24 h. Serial processing of the ¹H spectra was done using the TopSpin software.

Estimate of monomer reactivity ratios.

Given the discrepancies between the rate of polymerisation of DEGMA and MAA, in addition to the observed compositional drift during polymerisation, we estimated the reactivity ratio of the above sets of monomer pairs to determine whether or not the copolymers are truly statistical copolymers. In most cases, the instantaneous copolymer composition of a chain copolymerisation can be described by the terminal model of copolymerisation, otherwise known as the Mayo-Lewis methodology.¹⁻³ This model assumes that the reactivity of the propagating chain is only dependent on the monomer at the growing chain end. The relationship between the instantaneous composition of the monomer mixture to the copolymer composition can be described by the approximation as shown in Equation S1, when low conversion is reached. In order to obtain reliable results, it is frequently necessary to run the copolymerisation at different initial monomer ratios, although one initial feed ratio can also be used to approximate reactivity ratios using this method.^{4,5} Given that the aim of this study was to investigate the multiple stimuli-responsive properties of these polymers, combined with the fact that the conditions of the *in situ* NMR experiments deviated from the batch polymerisation experiments, we believe that conducting a full experiment with all of the required experiments is outside of the scope of this paper. Therefore, in this case we utilized the well-known integrated form of the copolymerisation equation (Eq. S1) to calculate the reactivity ratios r_1 and r_2 for monomers M1 (DEGMA) and M2 (MAA or DMAEMA), respectively:²

$$r_1 = \frac{\log \left[\frac{[M2_0]}{[M2_t]} \right] - \frac{1}{p} \log \left[\frac{1 - p \left[\frac{[M1_t]}{[M2_t]} \right]^2}{1 - p \left[\frac{[M1_0]}{[M2_0]} \right]^2} \right]}{\log \left[\frac{[M1_0]}{[M1_t]} \right] + \log \left[\frac{1 - p \left[\frac{[M1_t]}{[M2_t]} \right]^2}{1 - p \left[\frac{[M1_0]}{[M2_0]} \right]^2} \right]} \quad (S1)$$

$$p = \frac{1 - r_1}{1 - r_2} \quad (S2)$$

where $M1_0$ and $M2_0$ are monomers M1 and M2 at $t=0$ h, and $M1_t$ and $M2_t$ are monomers M1 and M2 at time (t) where polymerisation is stopped (<20% conversion); and p is an arbitrary value (and was -1 in this case). The values $M1_0$, $M2_0$, $M1_t$ and $M2_t$ were all determined experimentally from the above ^1H NMR experiments and used to solve Equations S1 and S2. The values obtained from this analysis are $r_1 = 1.46$ and $r_2 = 0.54$ for DEGMA:MAA, respectively and $r_1 = 1.02$ and $r_2 = 0.98$ for DEGMA:DMAEMA, respectively.

GPC traces.

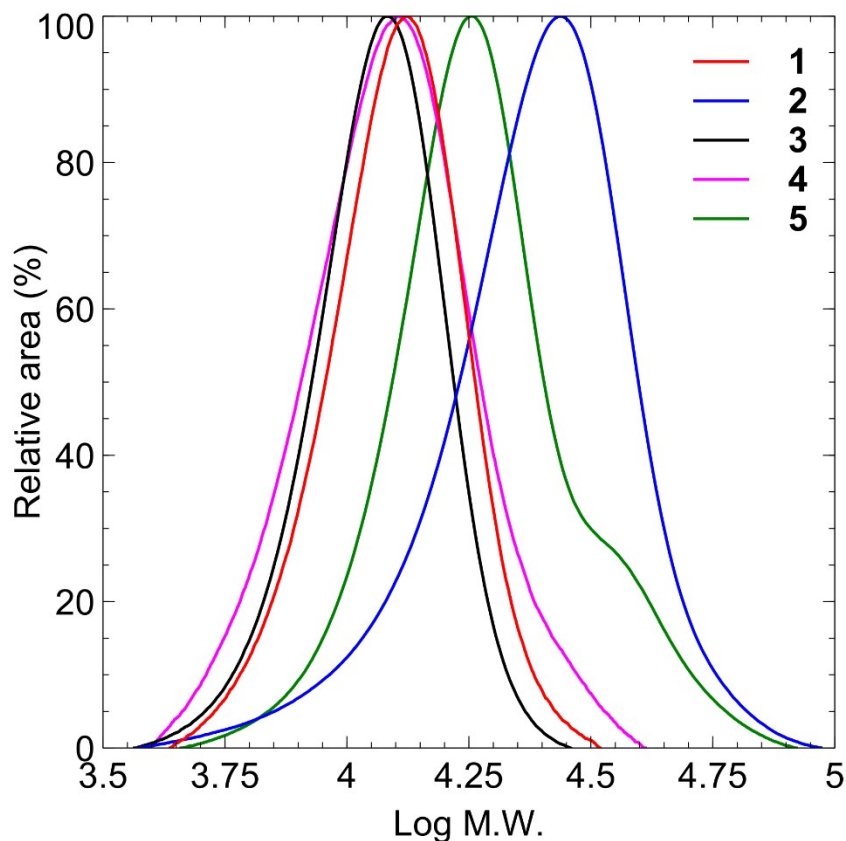


Figure S1. GPC traces of polymers 1-5. (Solvent: DMAc; M_n are relative to PMMA standards)

NMR spectra.

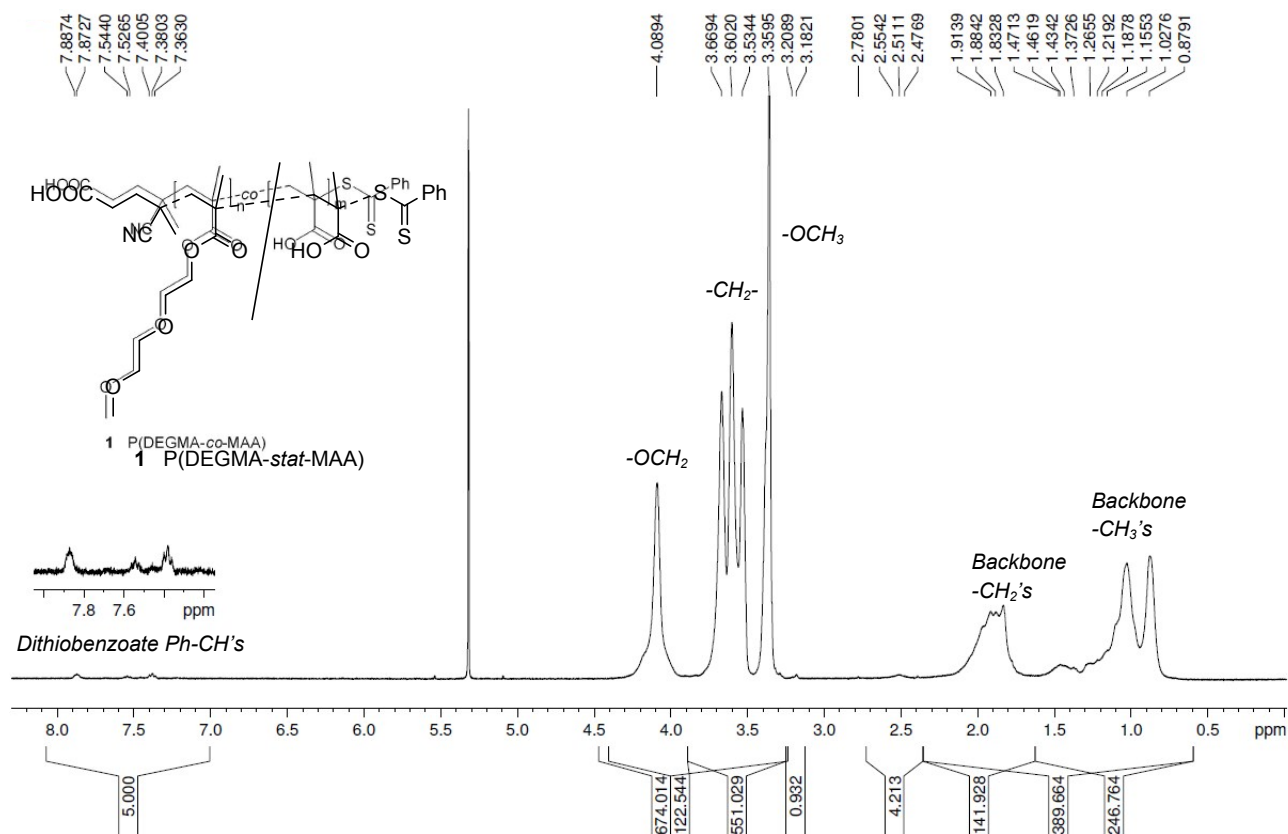


Figure S2. 1H NMR spectrum of P(DEGMA-*stat*-MAA) (1; CD_2Cl_2).

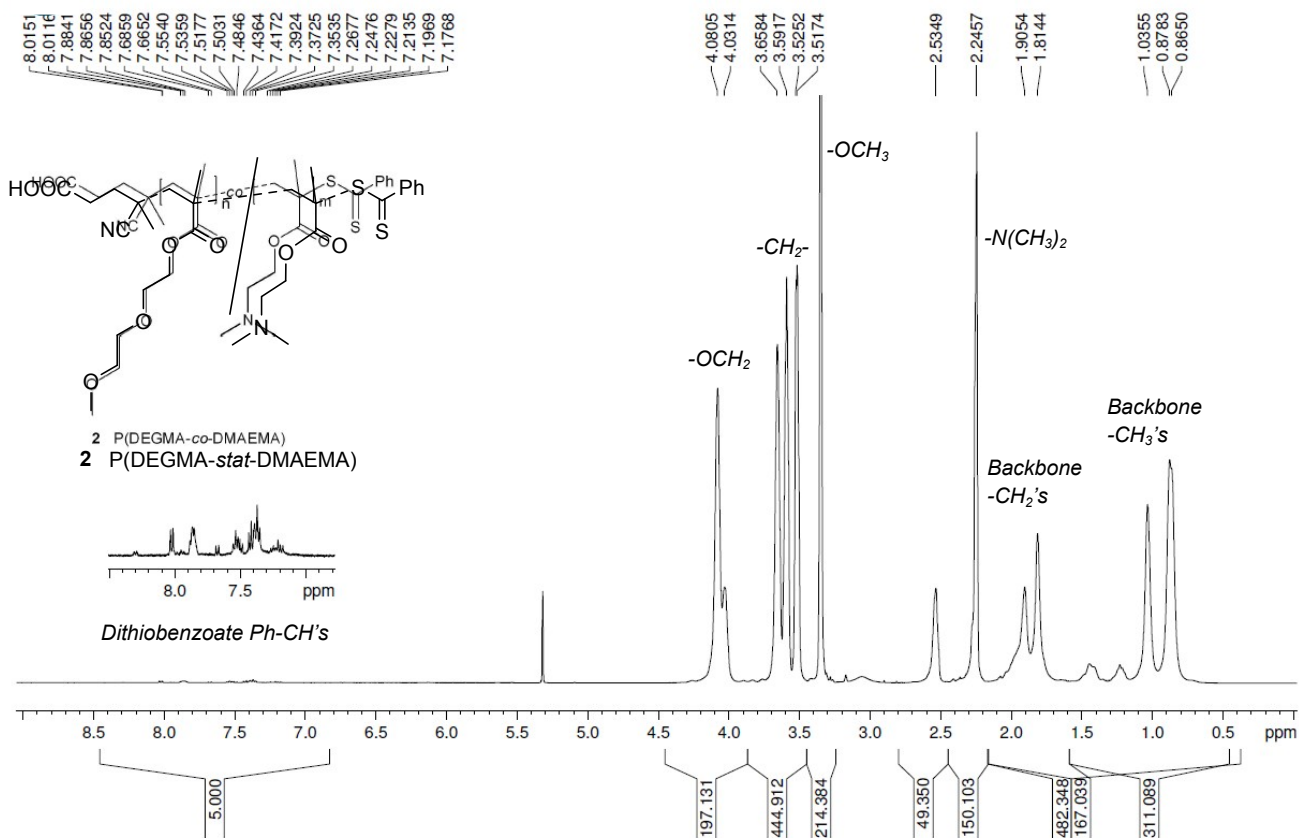


Figure S3. 1H NMR spectrum of P(DEGMA-*stat*-DMAEMA) (2; CD_2Cl_2).

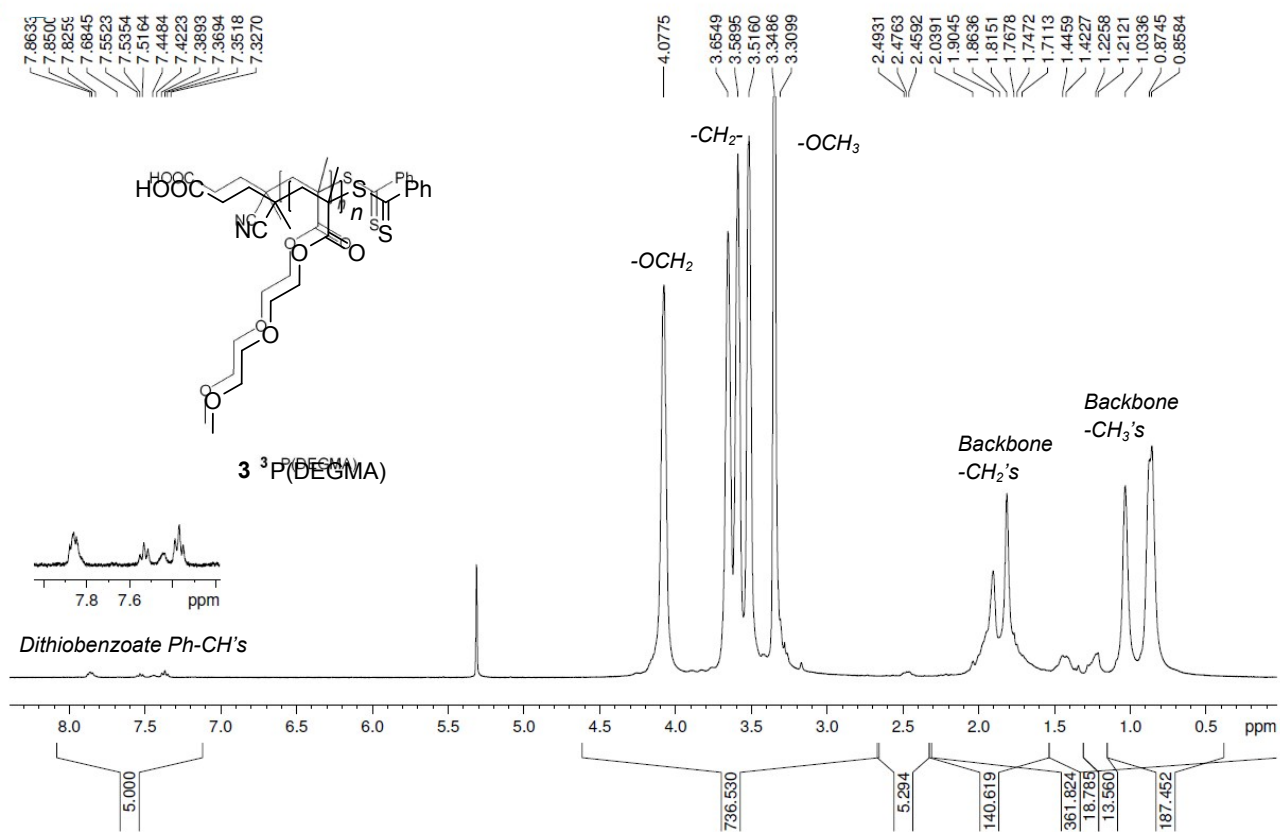


Figure S4. ^1H NMR spectrum of P(DEGMA) macroRAFT-CTA (**3**; CD_2Cl_2).

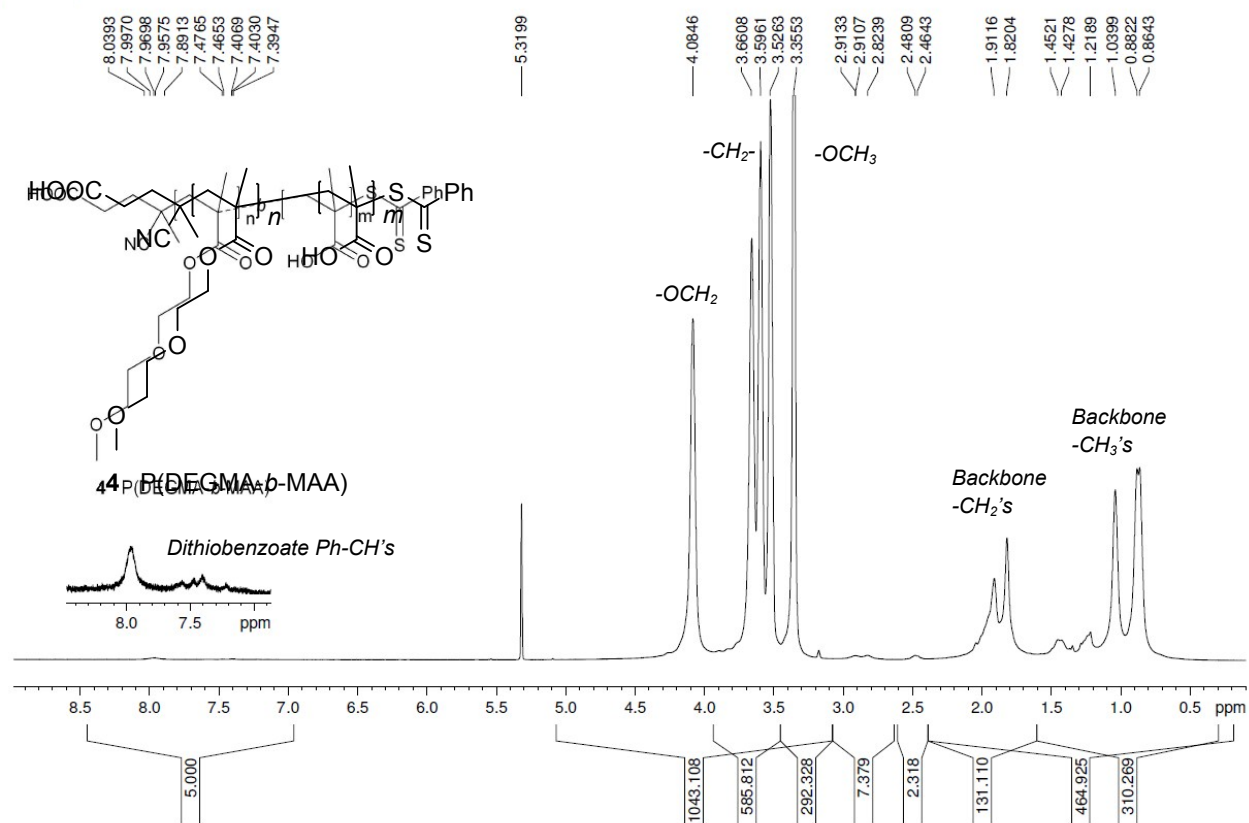


Figure S5. ^1H NMR spectrum of P(DEGMA-*b*-MAA) (**4**; CD_2Cl_2).

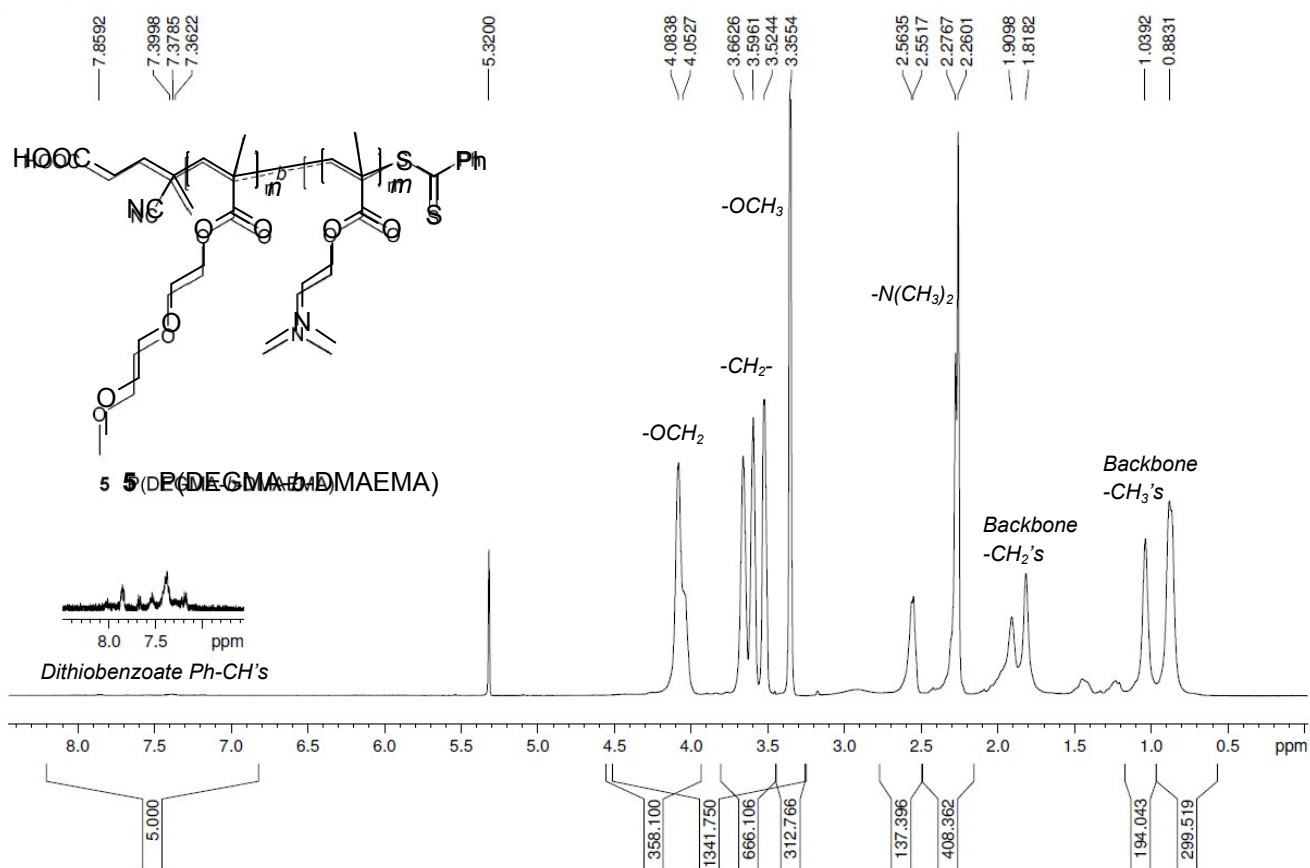


Figure S6. ^1H NMR spectrum of P(DEGMA-*b*-DMAEMA) (5; CD_2Cl_2).

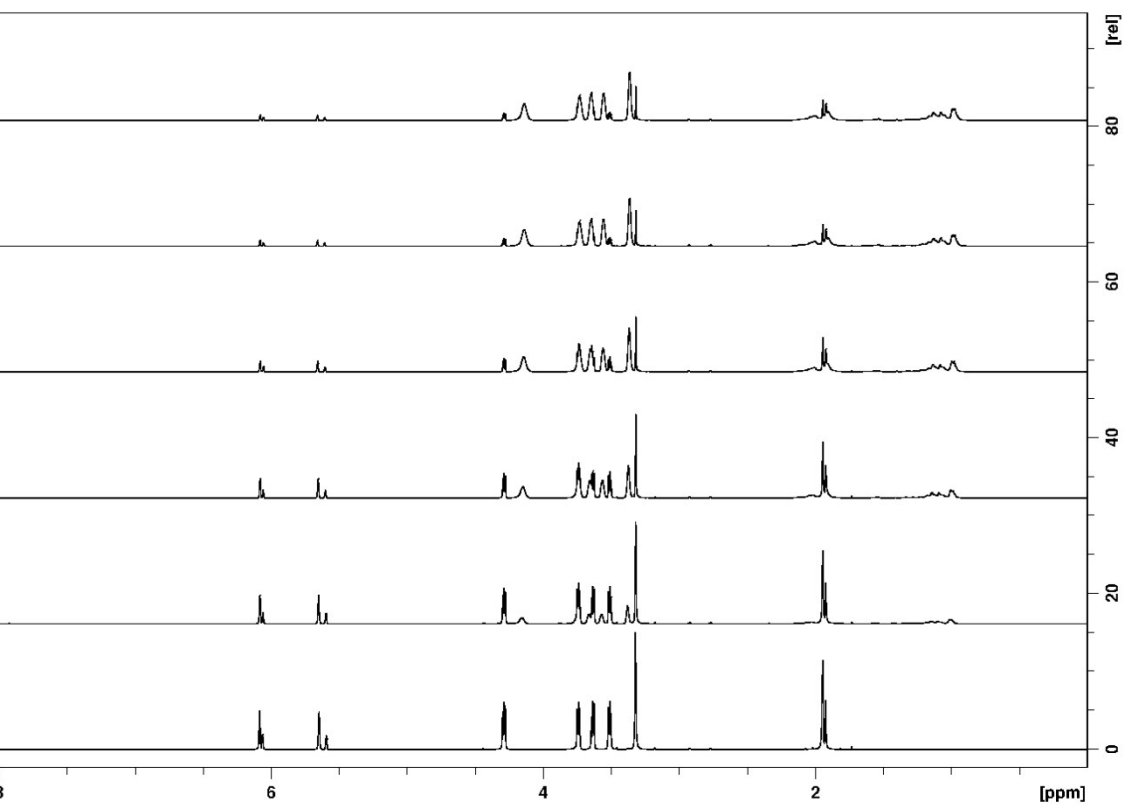


Figure S7. Overlay of ¹H NMR spectra of P(DEGMA-*stat*-MAA) (1*₁; DMF-*d*₇) at time 0, 2, 4, 8, 16, 24 hours (*bottom to top*, respectively).

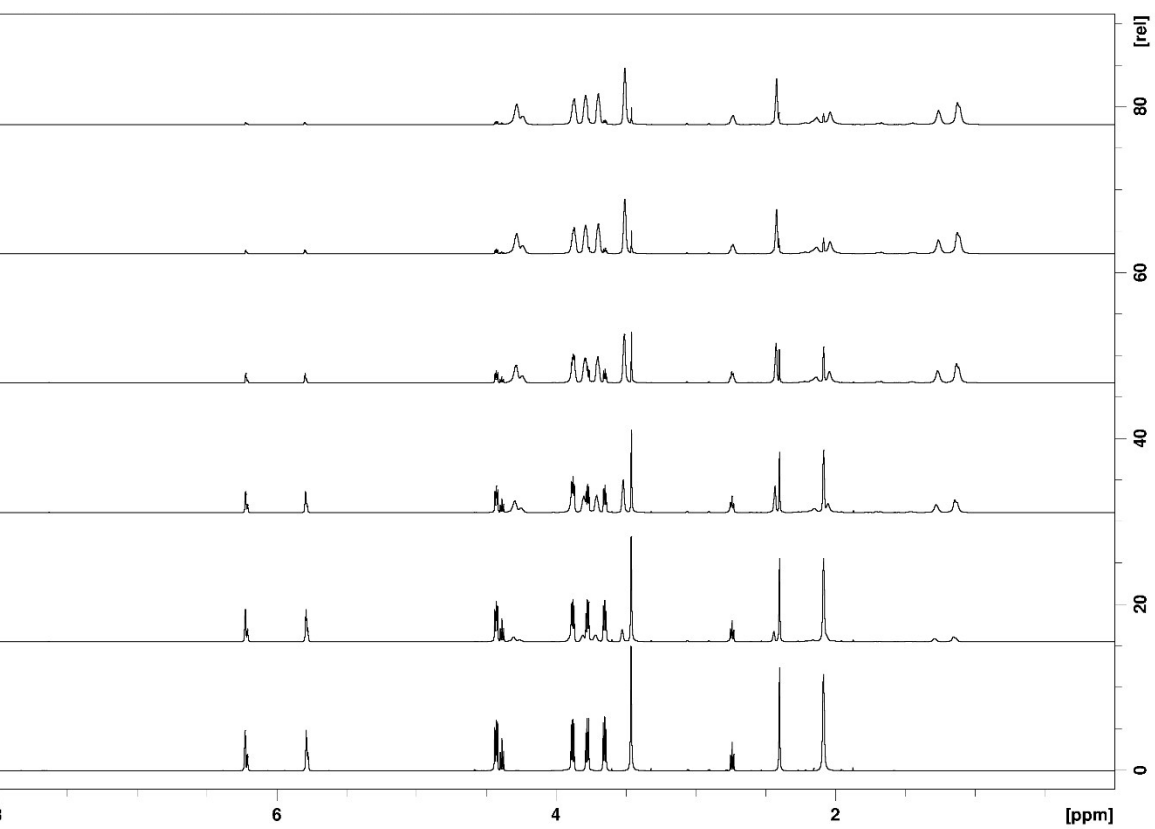


Figure S8. Overlay of ¹H NMR spectra of P(DEGMA-*stat*-DMAEMA) (2*); DMF-*d*₇) at time 0, 2, 4, 8, 16, 24 hours (*bottom to top*, respectively).

DLS Measurements

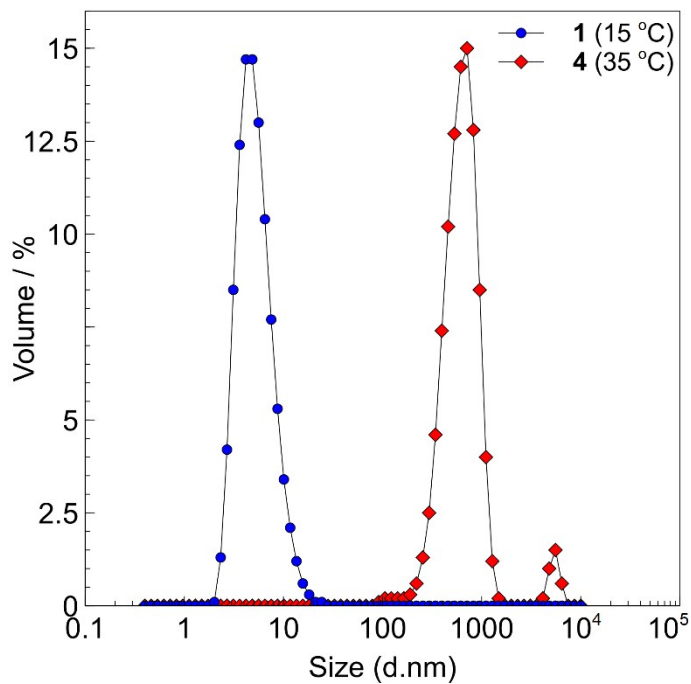


Figure S9. DLS measurements at specified temperatures of **3** P(DEGMA). Polymer solution was 2.5 mg mL⁻¹ in water, with measurements collected at 5 °C temperature intervals, over a 5-50 °C range. Specific values reported here correspond to temperatures below and above the specific polymer LCST for 2.5 mg mL⁻¹ solutions, as shown in Table S1.

Table S1. LCSTs and transition windows of a 2.5 mg mL⁻¹ solution of polymer **3** in Milli-Q water as measured by UV-Vis spectroscopy and DLS, respectively.

Polymer	UV-Vis ^a	DLS ^b
3	27	25-30

^a 5-70 °C range, 1 °C min⁻¹, 3 heating/cooling cycles; ^b 15-60 °C range, 5 °C min⁻¹, 1 heating/cooling cycle

References

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