Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information:

Influence of Architectural Design on the Thermoresponsive Properties of Pyrrolidone-Based Terpolymers

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1. ^{1}H NMR spectrum of NMEP monomer

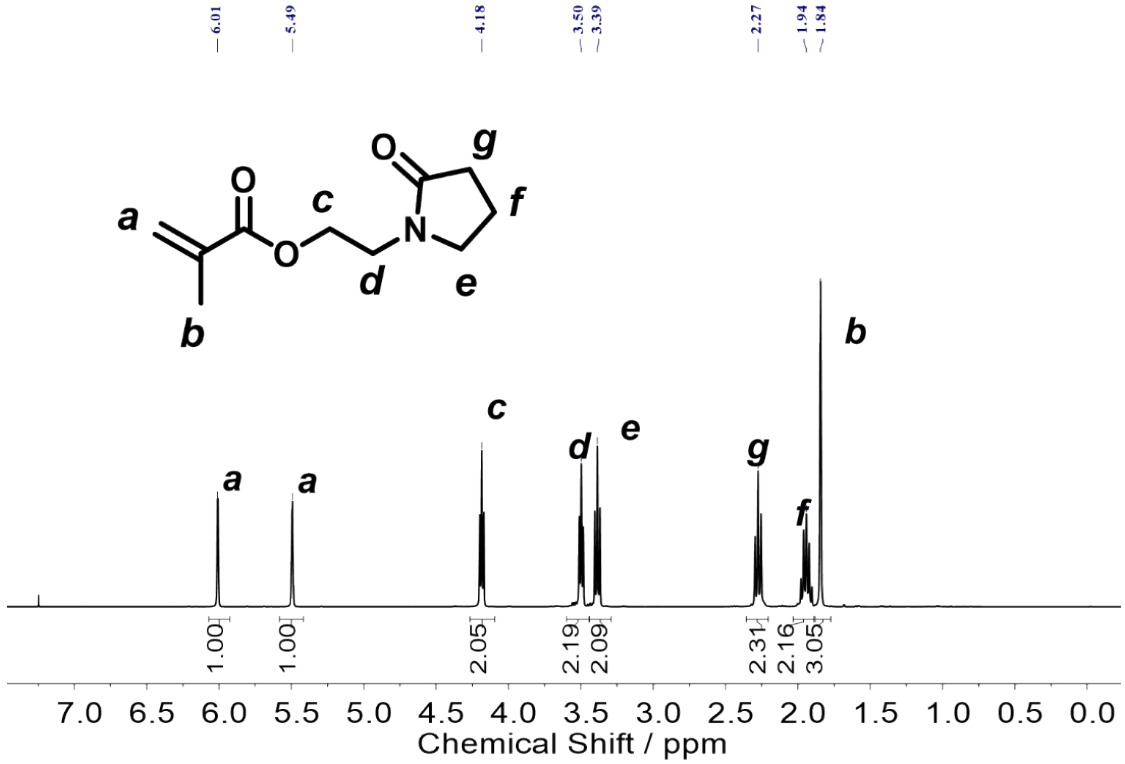

Figure S1. The molecular structure and ^{1}H NMR spectrum of *N*-(2-(methacryloyloxy)ethyl)pyrrolidone, as observed in $CDCl_3$

2. DP calculation of the PMMA macro-CTA

The average polymerisation degree ***n*** for the macro-CTA was estimated based on the integral areas (*I*) of the signals at δ = 3.55–3.60 ppm of protons **Hc** ((C=O)OC**H**$_3$) and at δ = 7.30-8.00 ppm of **H$_{d1}$, H$_{d2}$** and **H$_{d3}$** protons (-CS_2C_6**H**$_5$), using the following equations:

$$n = \frac{5 \times I_{3.55-3.60}}{3 \times I_{7.30-8.00}}$$

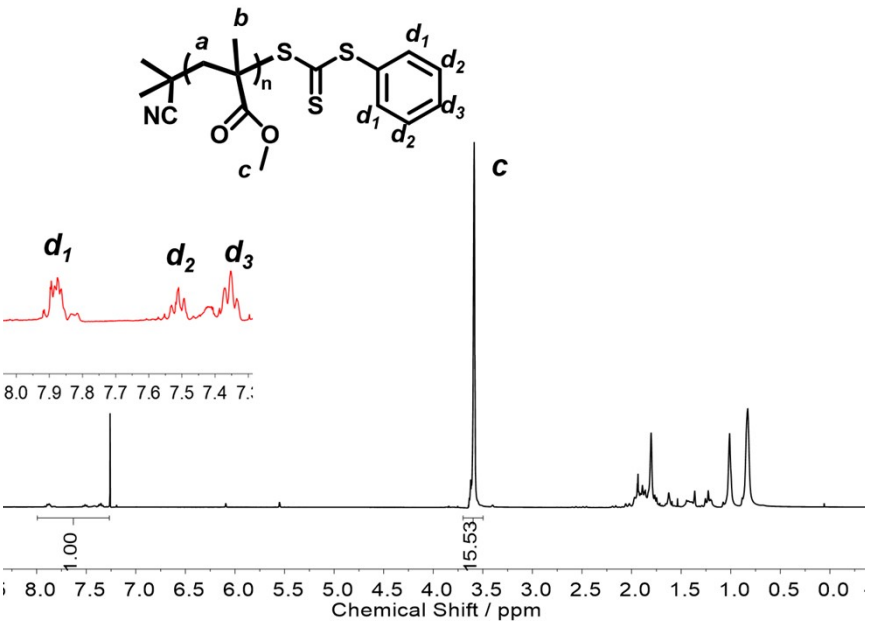

Figure S2. The molecular structure and ^{1}H NMR spectrum of $PMMA_{22}$ macro-CTA extracted from the reaction system. The insert image shows the ^{1}H NMR spectrum of the aromatic moiety of the macro-CTA.

3. DP calculation of the PDMAEMA macro-CTA

The average polymerisation degree ***n*** for the macro-CTA was estimated based on the integral areas (*I*) of the signals at δ = 3.95-4.15 ppm of protons **Hc** (-(C=O)OC**H**$_2$CH$_2$) and at δ = 7.30-8.00 ppm of $\mathbf{H_{d1}}$, $\mathbf{H_{d2}}$ and $\mathbf{H_{d3}}$ protons (-$CS_2C_6\mathbf{H}_5$), using the following equations:

$$n = \frac{5 \times I_{3.95-4.15}}{2 \times I_{7.30-8.00}}$$

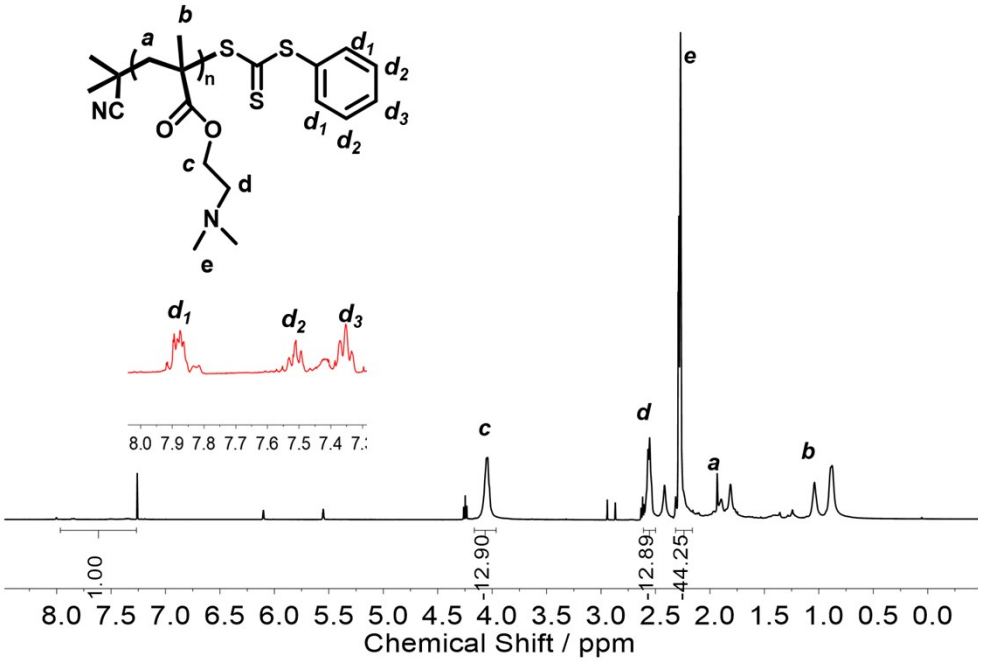

Figure S3. The molecular structure and ^{1}H NMR spectrum of PDMAEMA$_{32}$ macro-CTA extracted from the reaction system. The insert image shows the ^{1}H NMR spectrum of the aromatic moiety of the macro-CTA.

4. RAFT polymerisation conditions and ratios of C1-C4

Table S1. Experimental polymer structures, reaction ratios, and reaction conditions for C1-C4

No.	Experimental polymer structure[a.]	Ratio	Solvent	Temp (°C)	Time (h)
C1	DMA_{32}	[DMA]:[CPDB]:[AIBN] = 35:1:0.1	DMF	70	12
	DMA_{32}-*b*-MMA_{25}	[MMA]:[macro-CTA]:[AIBN] = 25:1:0.15	DMF	70	24
	DMA_{32}-*b*-MMA_{25}-*b*-$NMEP_{20}$	[NMEP]:[macro-CTA]:[AIBN] = 20:1:0.15	1,4-dioxane	70	24
C2	MMA_{22}	[MMA]:[CPDB]:[AIBN] = 25:1:0.1	DMF	70	12
	MMA_{22}-*b*-DMA_{31}	[DMA]:[macro-CTA]:[AIBN] = 35:1:0.15	DMF	70	24
	MMA_{22}-*b*-DMA_{31}-*b*-$NMEP_{18}$	[NMEP]:[macro-CTA]:[AIBN] = 20:1:0.15	1,4-dioxane	70	24
C3	MMA_{21}	[MMA]:[CPDB]:[AIBN] = 25:1:0.1	DMF	70	12
	MMA_{21}-*b*-$NMEP_{18}$	[NMEP]:[macro-CTA]:[AIBN] = 20:1:0.15	1,4-dioxane	70	24
	MMA_{21}-*b*-$NMEP_{18}$-*b*-DMA_{34}	[DMA]:[macro-CTA]:[AIBN] = 35:1:0.15	DMF	70	24
C4	MMA_{21}-*co*-$NMEP_{16}$-*co*-DMA_{27}	[MMA]:[NMEP]:[DMA]:[CPDB]:[AIBN] = 25:20:35:1:0.15	1,4-dioxane	70	24

[a.] Abbreviations: NMEP, DMA, and MMA correspond to *N*-(2-(methacryloyloxy)ethyl)pyrrolidone, 2-(dimethylamino)ethyl methacrylate and methyl methacrylate, respectively. It is noted that while 2-(dimethylamino)ethyl methacrylate is commonly referred to as DMAEMA, within this table, we further abbreviate it to DMA for ease of format.

5. ^{1}H NMR results of PNMEP-based terpolymers

The experimental composition for each block was determined through ^{1}H NMR, with distinctive peaks assigned to each comonomer: (i) for PMMA, the distinctive peak appears with proton resonance signals at δ = 3.55–3.60 ppm (-(C=O)OC**H**$_3$), (ii) for PNMEP, the distinctive peak is observed with proton resonance signals at around δ = 2.00–2.13 ppm (-N(C=O)CH$_2$C**H**$_2$CH$_2$), (iii) for PDMAEMA, the distinctive peak is seen at around δ = 2.53–2.70 ppm (-(C=O)OCH$_2$C**H**$_2$). The average polymerisation degrees *x, y, z* for PMMA$_x$-*b*-PDMAEMA$_y$-*b*-PNMEP$_z$ were calculated by the following equations, based on the integral areas (*I*) of the signals from each distinctive peak:

$$x = \frac{2 \times I_{3.55-3.60}}{3 \times I_{2.53-2.70}} \times y = \frac{2 \times I_{3.55-3.60}}{3 \times I_{2.00-2.13}} \times z$$

and $$M_{n=} 221.34 + x \times 100.12 + y \times 157.21 + z \times 197.23$$

where 221.34, 100.12, 157.21, and 197.23 represent the molar masses of RAFT chain transfer agent CPDB, MMA monomer, DMAEMA monomer, and NMEP monomer, respectively.

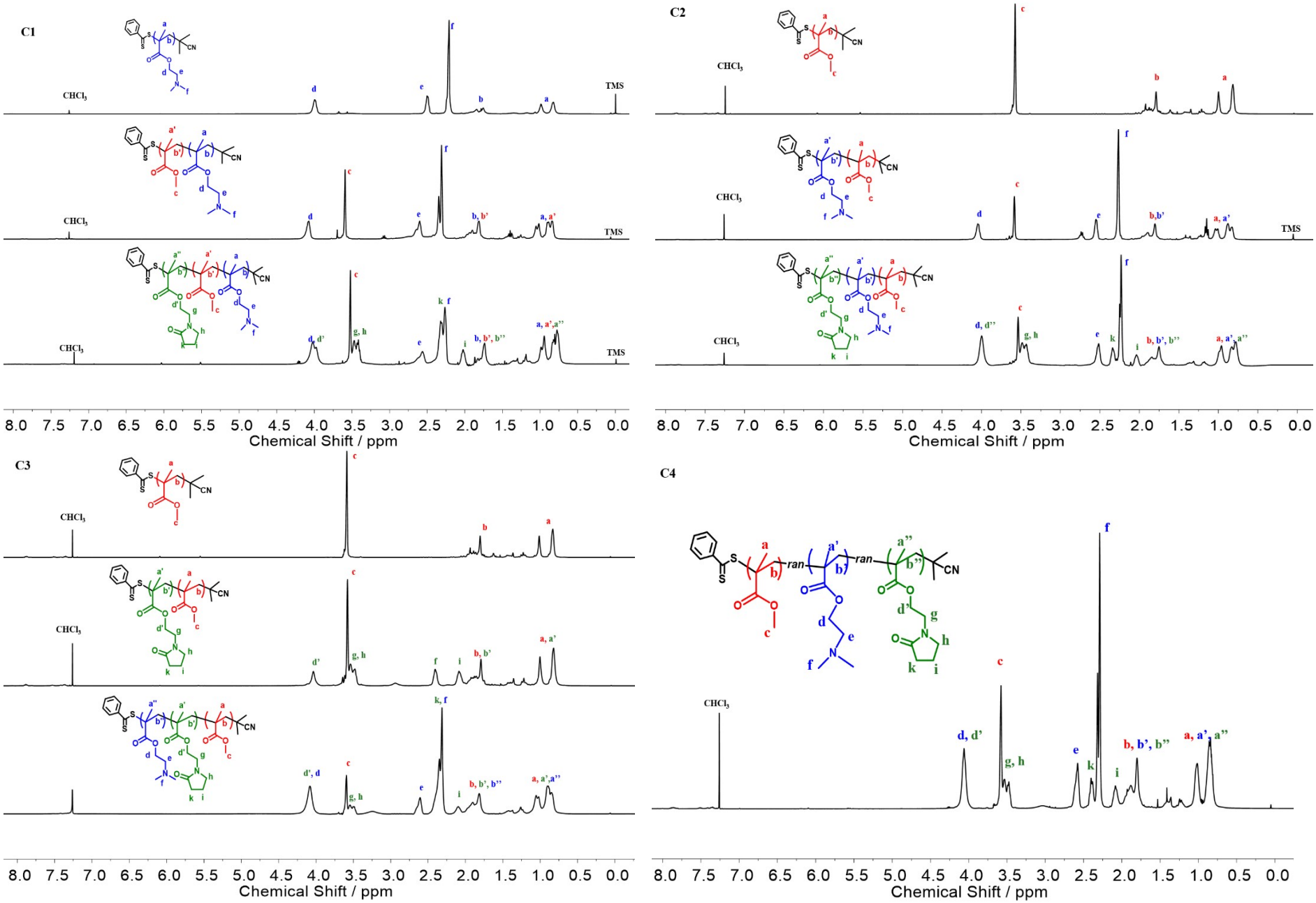

Figure S4. The ^{1}H NMR spectra of the triblock terpolymers C1 (top left), C2 (top right) and C3 (bottom left) and the statistical terpolymer C4 (bottom right).

6. Size Exclusion Chromatography (SEC) traces

Figure S5 depicts the triblock terpolymers and statistical terpolymers. The complete shift to the right of the GPC traces within the triblock terpolymers confirms the successful chain extension of the second and third blocks onto the macro-CTA.

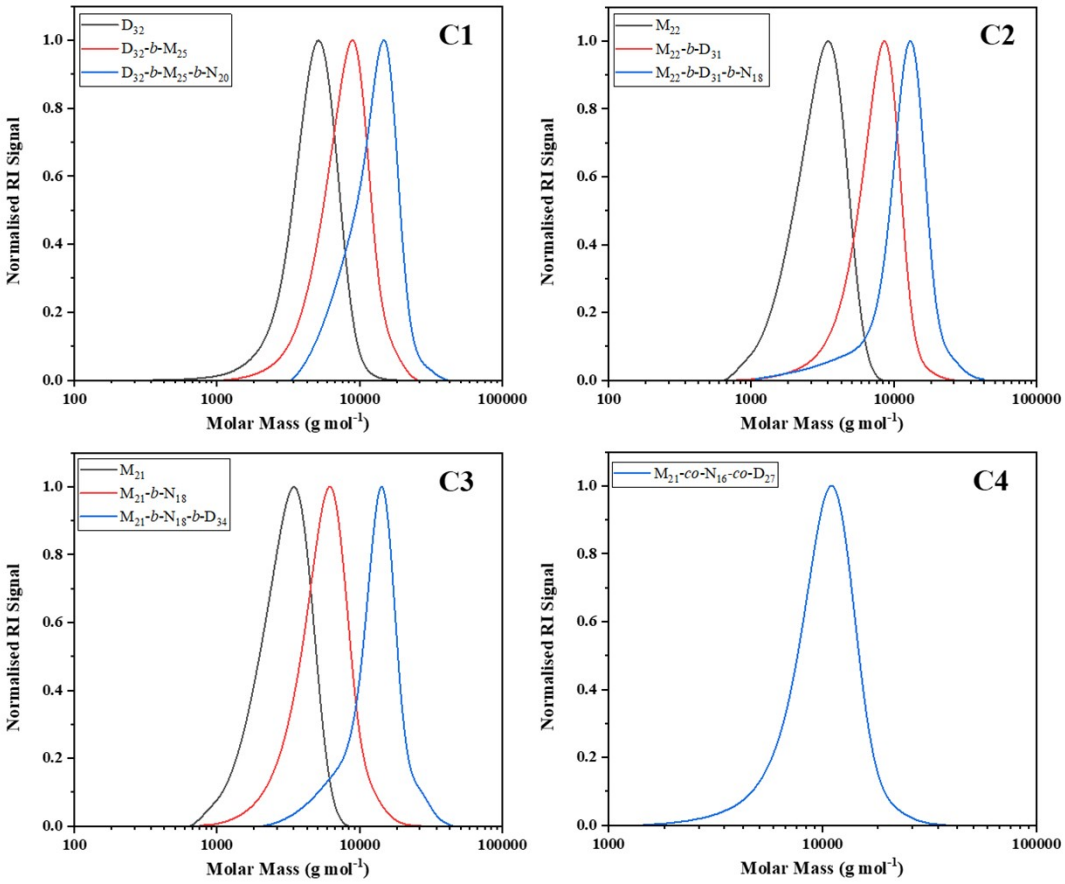

Figure S5. SEC traces of both the triblock and statistical terpolymers (sample C1-C4). For the triblock terpolymers, the lines in black, red, and blue represent the macro-CTA and the chain extension of the second and third blocks of C1 (top left), C2 (top right), and C3 (bottom left), respectively. D, M, N are the one-letter abbreviation of 2-(dimethylamino)ethyl methacrylate, methyl methacrylate, and *N*-(2-(methacryloyloxy)ethyl)pyrrolidone (NMEP), respectively.

7. Titration curve of the triblock terpolymer, $DMAEMA_{32}$-*b*-MMA_{25}-*b*-$NMEP_{20}$ (C1)

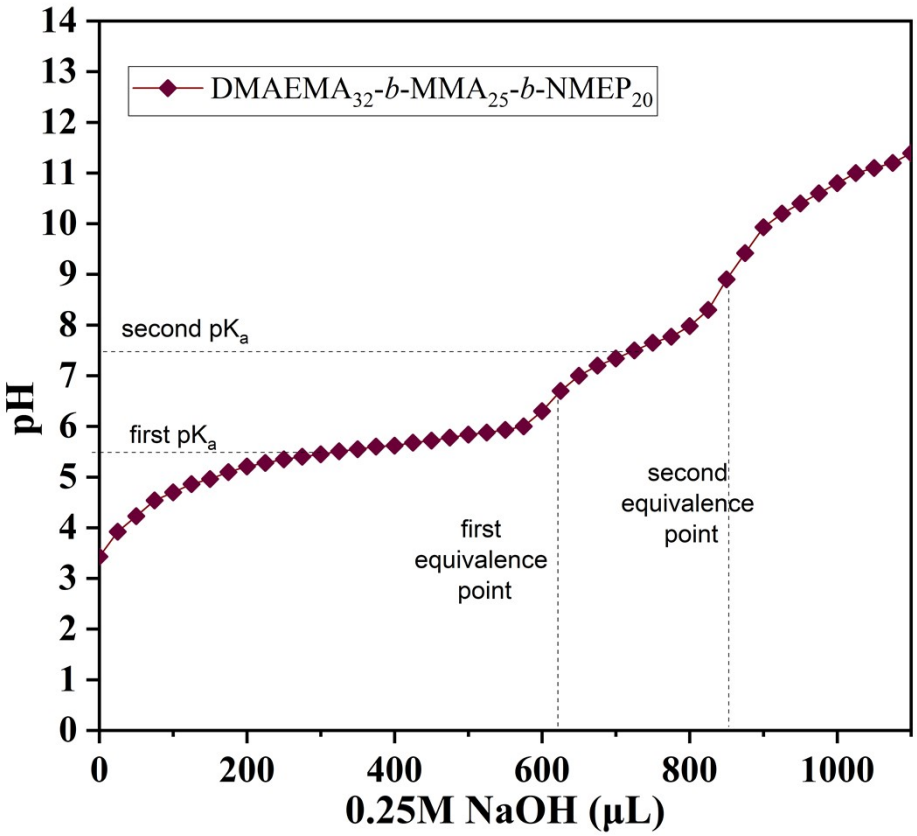

Figure S6. Titration curve of 1% w/w solution of $DMAEMA_{32}$-*b*-MMA_{25}-*b*-$NMEP_{20}$ (C1) in DI water, with the first and second pK_as identified in the figure.

8. DLS intensity distribution of C1-C4

DLS measurement was taken on 1% w/w polymer solution in DI water at room temperature (25℃) for C1 to C3 under 0% protonation, and at 10℃ for C4 under 10% protonation.

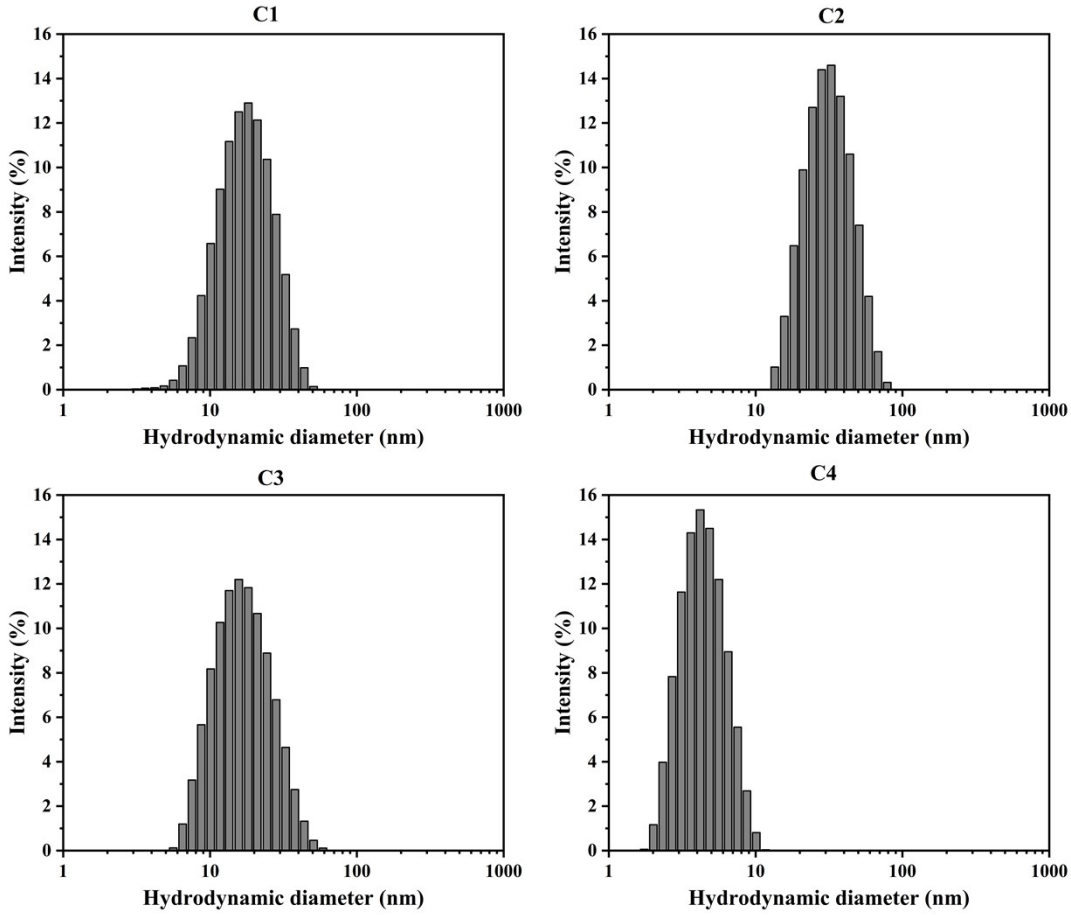

Figure S7. The particle size distribution of C1-C4, plotted as intensity against hydrodynamic diameter (D_h).

9. DLS temperature-ramping measurement on C1-C4

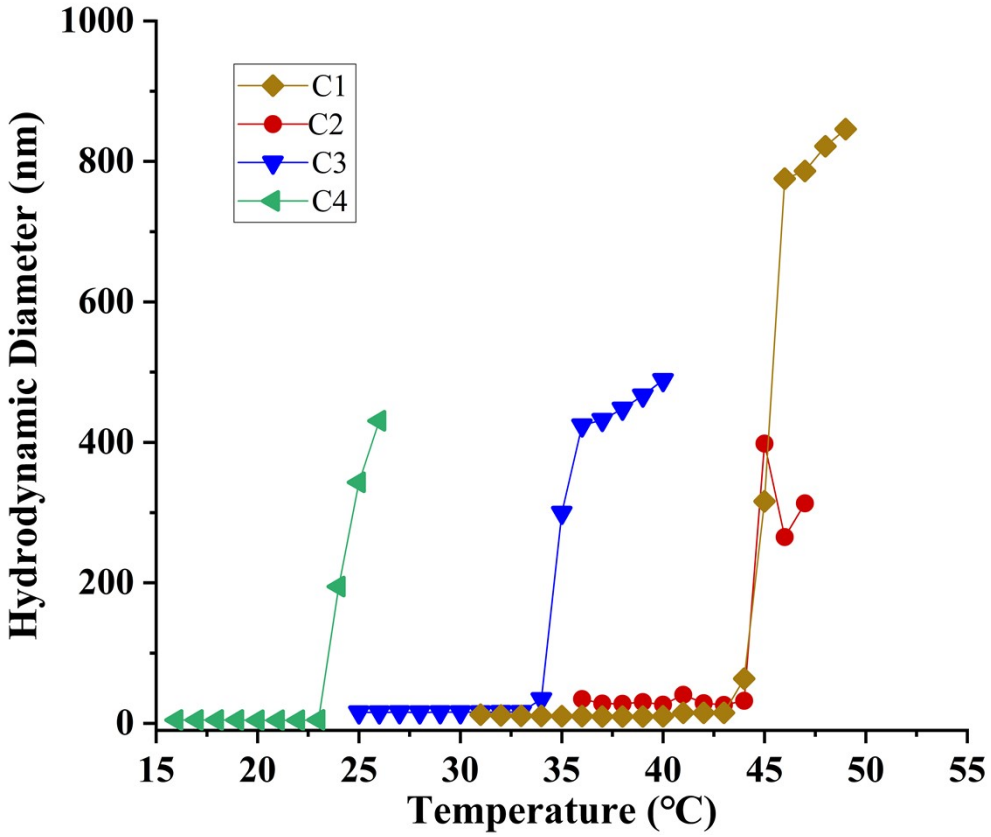

Figure S8. The change in hydrodynamic diameter with temperature for the terpolymers C1-C4, plotted from the DLS intensity distribution, measured at an increment of one °C near their respective transition temperatures.

10. Cloud point temperatures of PNMEP-based terpolymers

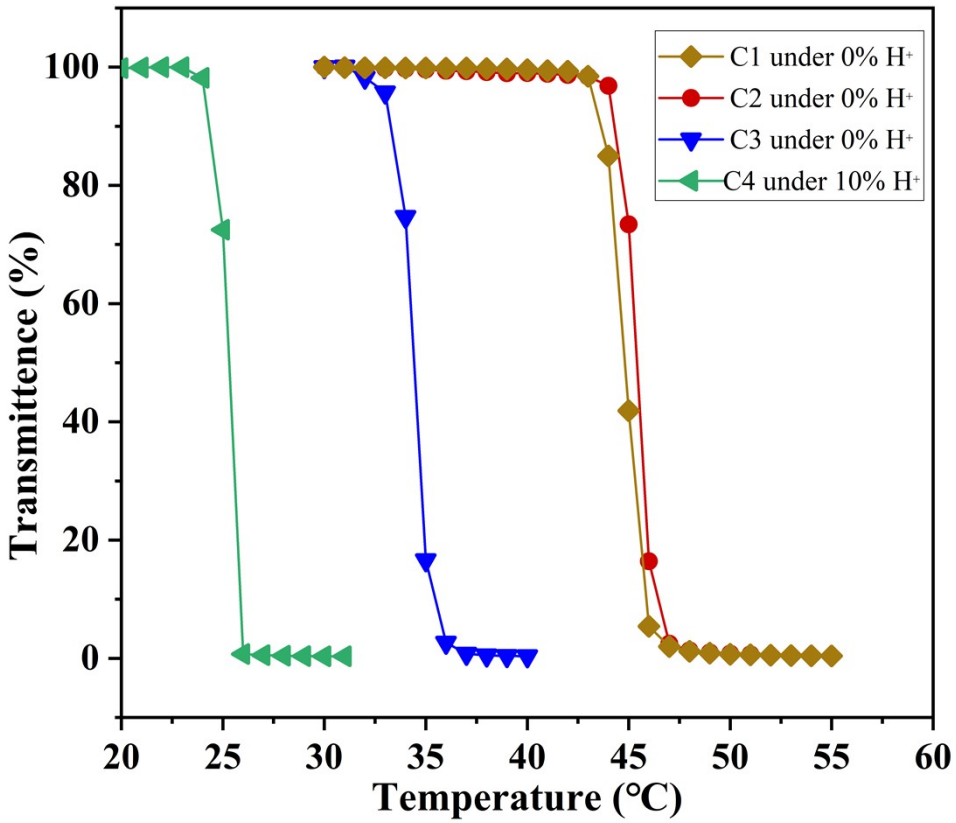

Figure S9. UV-transmittance curve plotted as a function of temperature, recorded on 1% w/w polymer solutions. The triblock terpolymer solutions (C1-C3) are under 0% protonation, and the statistical polymers are under 10% protonation.

11. 10% protonation calculation

The triblock terpolymers C1-C4 were evaluated for their change in cloud point temperatures under **10%** protonation. To achieve this, **5 g** of polymer solutions in DI water at a concentration of **1% w/w** were titrated with 1M HCl. The volume of 1M HCl required to be added to the polymer solution was calculated as follows:

$$n = \left(\frac{5 \times 1\%\ w/w \times\ comp\%_{NMEP}}{197.23} + \frac{5 \times 1\%\ w/w \times comp\%_{DMAEMA}}{157.21} \right) \times 10\%$$

and

$$v_{HCl}(measured\ in\ \mu L) = \frac{n}{conc_{HCl}} \times 10^6 = \frac{n}{1 mol/L} \times 10^6$$

The compositions of the amine-based comonomer contents were determined by ^{1}H NMR. Here, 5g represents the mass of the polymer solution, and 197.23 g/mol and 157.21 g/mol represent the molar masses of the NMEP and DMAEMA monomers, respectively.