Supporting Information

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Thermoresponsive Triblock-Copolymers of Polyethylene Oxide and Polymethacrylates: Linking Chemistry, Nanoscale Morphology, and Rheological Properties

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Supplementary information

1. Experimental Section

1.1 Materials

N-isopropyl acrylamide (NIPAM) (97 %), 2-N-(dimethylamino)ethyl methacrylate (DMAEMA) (98 %), tetrahydrofuran (THF) (99 %), triethylamine (TEA) (99.5 %) and diethylene glycol methyl ether methacrylate (DEGMEMA) (95 %) were purchased from Sigma-Aldrich (U.K.). Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) (99 %) and 2- bromoisobutyryl bromide (BiBB) (97 %) were purchased from Alfa Aesar (U.K.). Isopropyl alcohol (IPA), (99 %) absolute ethanol (EtOH) (99 %), methanol (MeOH) (99%) and dichloromethane (DCM) (99 %) were purchased from Fisher Scientific (U.K.). Bipyridine (BPY) (99 %), dimethylamino pyridine (DMAP) (97 %) and polyethylene glycol (PEG) 10 kDa were purchased from Aldrich (U.K.). PEG 5 kDa was purchased from Fluka (U.K.). 5 and 10 kDa PEGs were found to have molecular weights of 5.4 and 10.8 kDa by ¹H NMR, respectively. Brockmann I neutral alumina was purchased from Acros Organics (U.K.). Dialysis tubing with a molecular weight cut off (MWCO) ~ 3500 D₈72a was purchased from Medicell Membrane Ltd (U.K.) and soaked in deionised H₂O before use. GPC EasiVial poly(methyl methacrylate) mixed standards and poly(methyl methacrylate) single standard (72 kDa) were purchased from Agilent (U.K.). Deionised H₂O was used in all experiments. All reagents were used as supplied, unless indicated otherwise.

Dulbecco’s Modified Eagle’s Medium - high glucose with 4500 mg/L glucose, L-glutamine, sodium pyruvate and sodium bicarbonate (DMEM), Fetal Bovine Serum (FBS), L-Glutamine and Penicillin-Streptomycin (Pen-Strep) were purchased from Sigma (U.K.) and used as purchased. CytoTox-ONE™ Homogeneous Membrane Integrity Assay (LDH) and CellTiter 96® AQueous One Solution Cell Proliferation Assay (MTS) were purchased from Promega (U.K.) and used as guided in the protocol.

1.2 Methods

1.2.1 Synthesis of the 5 and 10 kDa PEG macroinitiators
PEG macroinitiators were synthesised at two molecular weights; targeting 5 kDa and 10 kDa using the procedure outlined by Garcia et al. (2015). DMAP (1.17 g, 9.6 mmol) in DCM (8 mL) was mixed with TEA (0.89 mL, 6.4 mmol) and cooled to 0 °C. BiBB (1.97 mL, 16.0 mmol) in DCM (8 mL) was added to the DMAP and TEA solution. A solution of PEG (10 kDa, 16.0 g; or 5 kDa, 6.4 g; 1.6 mmol) in DCM (160 mL) was then added dropwise over 1 h. When the PEG addition finished, the reaction was allowed to rise to room temperature and stirred for 18 h. The solution was filtered, and approximately half of the solvent removed in vacuo. The crude PEG initiator was then precipitated in cold diethyl ether (480 mL) and filtered. The solid was then recrystallised from absolute ethanol (300 mL) overnight. The recrystallised solid was then filtered and washed with cold diethyl ether, before drying in vacuo to yield pure PEG macroinitiator.

1.2.2 Synthesis of ABA triblock copolymers

Triblock copolymers were synthesised by atom transfer radical polymerisation from PEG macroinitiators using prediction of molecular weight based on pilot conversions to synthesise homopolymers (data not shown). A typical procedure is given, with the specific conditions in Table S1. The macroinitiator, ligand and monomer were dissolved in solvent and the flask sealed, followed by bubbling with nitrogen for 30 min to degas the mixture. The Cu(I)Br catalyst was placed in a separate flask and sealed before degassing with nitrogen bubbling for 30 min. The solvent solution was then transferred to the Cu(I)Br vessel via a degassed syringe and was allowed to react under constant stirring for 48 h at a constant temperature. The reaction solvent was then evaporated in vacuo, the product redissolved in THF, and the mixture passed through Brockmann I neutral alumina to remove the copper-ligand complex. The THF was removed in vacuo, and the crude product dissolved in DI H₂O and dialysed for 48 h using a dialysis membrane with molecular weight cut off 3500 Da to remove any residual copper. After dialysis the solution was freeze dried yielding pure polymer (Table S1).
Table S1: Reagents, quantities conditions used to synthesise the tri-block copolymers and percentage yield obtained for each.

| Tri-block Copolymer | Monomer (Quantity) | Initiator (Quantity) | Catalyst (Quantity) | Ligand (Quantity) | Solvent (Quantity) | Temp (°C) | Yield (%) |
|---------------------|--------------------|----------------------|---------------------|-------------------|--------------------|-----------|-----------|
| N10-P5-N10          | NIPAM (4.2 g, 37.1 mmol) | PEG5kDa (0.5 g, 125 µmol) | CuBr (35.9 mg, 250 µmol) | Me6TREN (66.8 µL, 250 µmol) | DI Water (10 mL) | RT | 91.2      |
| N10-P10-N10         | NIPAM (4.0 g, 35.3 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuBr (28.7 mg, 200 µmol) | Me6TREN (53.5 µL, 200 µmol) | DI Water (10 mL) | RT | 90.3      |
| N20-P10-N20         | NIPAM (6.0 g, 53.0 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuBr (28.7 mg, 200 µmol) | Me6TREN (53.5 µL, 200 µmol) | DI Water (10 mL) | RT | 89.5      |
| D10-P5-D10          | DMAEMA (5.4 mL, 31.8 mmol) | PEG5kDa (0.5 g, 125 µmol) | CuCl (24.7 mg, 250 µmol) | Bipyridine (78.0 mg, 500 µmol) | MeOH (20 mL) | RT | 86.2      |
| D10-P10-D10         | DMAEMA (4.3 mL, 25.4 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuCl (19.8 mg, 200 µmol) | Bipyridine (62.5 mg, 400 µmol) | MeOH (20 mL) | RT | 90.0      |
| D20-P10-D20         | DMAEMA (6.4 mL, 38.2 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuCl (19.8 mg, 200 µmol) | Bipyridine (62.5 mg, 400 µmol) | MeOH (20 mL) | RT | 85.3      |
| DEG10-P5-DEGMEMA    | DEG10 (4.9 mL, 26.6 mmol) | PEG5kDa (0.5 g, 125 µmol) | CuBr (35.9 mg, 250 µmol) | Bipyridine (78.0 mg, 500 µmol) | iPA (20 mL) | 40 | 84.1      |
| DEG10               | DEG10 (3.9 mL, 21.3 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuBr (28.7 mg, 200 µmol) | Bipyridine (62.5 mg, 400 µmol) | iPA (20 mL) | 40 | 88.9      |
| DEG20-P10-DEGMEMA   | DEG10 (5.9 mL, 31.8 mmol) | PEG10kDa (1.0 g, 100 µmol) | CuBr (28.7 mg, 200 µmol) | Bipyridine (62.5 mg, 400 µmol) | iPA (20 mL) | 40 | 87.6      |
| DEG20 mL, 32.0 mmol) | 100 µmol) | µmol) | µmol) |
|----------------------|------------|--------|--------|


1.2.3 Polymer characterisation

All NMR spectroscopy was performed on an Oxford Instrument ECA600 600 MHz NMR spectrometer with Delta 4.3.6 software. PEG macroinitiators were characterised using $^1H$ NMR NMR in D$_2$O. Triblock copolymers were characterised using $^1H$ NMR and $^1H$ Diffusion Ordered Spectroscopy (DOSY) in CDCl$_3$.

An Agilent 12600 Infinity II gel permeation chromatography (GPC) instrument equipped with a refractive index (RI) detector was used to characterise the molecular weight distribution of both PEG macroinitiators and all synthesised triblock copolymers. The GPC used two columns; a Varian PLGel 5 μm mixed-D column and a Phenomenex Phenogel 10 μm 10E5 Å which were run in sequence. The GPC ran DMF with 0.1 % LiBr as an eluent, at a flow rate of 0.4 mL/min with the columns and RI detector held at 30 °C. The GPC was calibrated with Agilent Easivial poly(methyl methacrylate) (PMMA) standards with Mn ranging from 370 to 364000 Da (R$^2$: 0.9998).

1.2.4 Dynamic light scattering of triblock copolymers in aqueous solution

Dynamic light scattering (DLS) was performed using a Malvern Zetasizer Nano Series Nano – ZS with Zetasizer software at 1 mg/mL in aqueous solution as a function of temperature. The sample was heated from 25 to 70 °C in 5 °C increments, and at each temperature three measurements were taken. The micellization temperature was taken as the temperature at which the derived count rate increased.

1.2.5 Rheology of triblock copolymers in 20 % w/v aqueous solution

Rheology was performed on a TA AR 1500 ex rheometer with a Peltier unit using rheology advantage software. 20 % w/v aqueous solutions of triblock copolymers were prepared in DI H$_2$O and refrigerated overnight prior to analysis. Samples were analysed using a 40 mm parallel plate geometry with a 650 μm gap. Firstly, oscillatory stress sweeps were performed from 1 to 100 Pa with a frequency of 1 Hz in order to identify the linear viscoelastic region (LVR). Using an oscillatory stress from the LVR (1 Pa), temperature ramps were then performed from 15 to 70 ºC at a heating rate of 2 ºC per min and a frequency of 1 Hz. The
data is presented as the storage modulus (G’) and loss modulus (G’’) as a function of temperature.

1.2.6 Small-angle neutron scattering (SANS) measurements

SANS measurements were performed on the D22 instrument at the Institut Laue-Langevin (Grenoble, France). The neutron wavelength was set to 6 Å, the sample-detector distance at 2, 5.6, and 17.6 m, with collimator 2.8, 8, and 17.6, respectively. The detector offset was 300 mm. These settings resulted in a wave vector range $2.7 \times 10^{-3} \leq q \leq 0.45 \text{ Å}^{-1}$. Hellma cuvettes with a thickness of 1 mm were used for all samples. Measurements were performed at 25, 37, 40, and 50 °C with a minimum equilibration time of 15 min prior to sample run. Data reduction and stitching was performed on Igor Pro (Wavemetrics, USA) and data fitting was conducted using SasView 4.2.2 (http://www.sasview.org/). The scattering length densities (SLDs) were calculated from the monomeric unit using the Neutron activation and scattering calculator website from NIST center for neutron research (Neutron activation and scattering calculator).

The scattering intensity $I(q)$ can be written as follows:

$$I(q) = A(P(q)A S(q)_A + BKG$$

Where,

- $A$ is a proportionality constant,
- BKG is the background,
- $P(q)$ is the form factor of the scattering object,
- $S(q)_A$ is the corresponding structure factor

If more than one scattering object is present or the object studied has a hierarchical structure that generates scattering at distinct length scales, the expression can be extended to include further terms.

For this work, the polymer constructs, in general, give rise to two scattering signals, one arising from its supramolecular structures and the other from the polymeric chains. Therefore, $I(q)$ is expressed as:
\[ I(q) = A(P(q)_A S(q)_A) + B(P(q)_{PGC}) + BKG \]

where

\( A \) and \( B \) are proportionality constants,

\( BKG \) is the background,

\( P(q)_A \) is the form factor for model A,

\( S(q)_A \) is the corresponding structure factor,

\( P(q)_{PGC} \) is the form factor for polydisperse polymer coils.\(^5\)

The model A varies depending on the ABA polymer studied as the different chemistries induce self-assembly into different shapes. More specifically, ellipsoids,\(^6\) spheres,\(^7\) core-shell spheres,\(^8\) cylinders,\(^9\) core-shell cylinders,\(^10\)\(^11\) flexible cylinders,\(^12\)\(^13\) and core-shell cylinders have been used.\(^12\)\(^13\) The models are described in detail elsewhere, but a brief description follows.

**Cylinders**

For cylinders:

\[ P(q) = P(q,R_{maj},\varepsilon,L,\sigma) = (F_{cs}^2(q,R_{maj},\varepsilon))P_{cylinder}(q,L) \]

where

\( R_{maj} \) is the major radius,

\( \varepsilon \) is the ellipticity of the cross ratio (\( \varepsilon=R_{min}/R_{maj} \)),

\( L \) is the length of the cylinders,

\[ F_{cs}(q,R_{maj},\varepsilon) = \frac{2}{\pi} \int_0^{\pi/2} 2J_1 \left( \frac{qR_{maj}(\sin^2\theta + \varepsilon^2\cos^2\theta)^{1/2}}{qR_{maj}(\sin^2\theta + \varepsilon^2\cos^2\theta)^{1/2}} \right) d\theta \]

Is the contribution of the elliptical cross-section,

\[ P_{cylinder}(q,L) = L^{2} \left( \frac{2Si(qL)}{qL} - \frac{4\sin^2 \left( \frac{qL}{2} \right)}{(qL^2)} \right) \]

Is the contribution from the cylinder’s length, where

\[ Si(x) = \int_x^{\infty} \frac{\sin u}{u} du \]

\( J_1 \), is a first order Bessel function and \( \sigma \) represents the cross-section length polydispersity.

The form factor for cylinders is the same as for elliptical cylinders with \( \varepsilon=1 \) (spherical cross-section).
Flexible-cylinders form factor can be obtained by using the form factor the cylinders replacing \( P_{\text{cylinder}} \) with:

\[
P_{\text{flexible}} = (q, L, L_{\text{Kuhn}})
\]

Where, \( L_{\text{Kuhn}} \) is the Kuhn length of the flexible cylinder.[14]

For core-shell cylinders:

\[
P(q) = \frac{\text{scale}}{V_\text{s}} F(q, \alpha) \sin(\alpha) + BKG
\]

Where,

\[
F(q, \alpha) = V_c (\rho_c - \rho_s) \frac{\sin \left( \frac{q}{2} L \cos \alpha \right)}{q \frac{1}{2} L \cos \alpha} 2J_1(qR \sin \alpha) \frac{qR \sin \alpha}{qR \sin \alpha} + V_s (\rho_s - \rho_{\text{solv}}) \frac{\sin \left( \frac{q}{2} L + T \cos \alpha \right)}{q \left( \frac{1}{2} L + T \right) \cos \alpha} 2J_1(q(R + T) \sin \alpha) \frac{q(R + T) \sin \alpha}{q(R + T) \sin \alpha}
\]

\[
V_\text{s} = \pi (R + T)^2 (L + 2T)
\]

\( \alpha \) is the angle between the cylinder and the \( q \) vector.

\( V_\text{s} \) is the cylinder’s volume,

\( V_c \) is the volume of the cylinder’s core,

\( R \) is the core’s radius,

\( T \) is the shell’s thickness,

\( \rho_c, \rho_s, \) and \( \rho_{\text{solv}} \), are the scattering length densities of the core, shell, and solvent, respectively.

\( J_1 \) is a first order Bessel function.

**Spheres**

The form factor for sphere is as follows:

\[
P(q) = \frac{\text{scale}}{V} F(q)^2 + BKG
\]

\[
F(q) = 3V \left( \Delta \rho \frac{\sin(qr) - qr \cos(qr)}{(qr)^3} \right)
\]

Where,

\( V \) is the volume of the sphere,

\( R \) the radius of the sphere,
\( \Delta \rho, \) is the scattering length difference between sphere and solvent.

For a core-shell sphere, \( F \) is replaced with:

\[
F(q) = \frac{3}{V_s} \left( V_c (\rho_c - \rho_s) \frac{\sin(qr_c) - qr_c \cos(qr_c)}{(qr_c)^3} + V_s (\rho_s - \rho_{solv}) \frac{\sin(qr_s) - qr_s \cos(qr_s)}{(qr_s)^3} \right)
\]

Where,
\( V_s, \) is the sphere volume,
\( V_c, \) is the core’s volume,
\( r_s, \) is the sphere radius,
\( r_c, \) is the core radius,
\( \rho_c, \rho_s, \) and \( \rho_{solv}, \) are the scattering length densities of the core, shell, and solvent, respectively.

**Ellipsoids**

For oriented ellipsoids:

\[
P(q, \alpha) = \frac{\text{scale}}{V} F^2(q, \alpha) + BKG
\]

Where,

\[
F(q, \alpha) = \Delta \rho V \frac{3(\sin qr - qr \cos qr)}{(qr)^3}
\]

\[
r = \left[ R_p^2 \sin^2 \alpha + R_e^2 \cos^2 \alpha \right]^{1/2}
\]

Where,
\( R_p, \) is the polar radius,
\( R_e, \) is the equatorial radius,
\( \alpha, \) is the angle between the ellipsoid and the \( q \) vector.

For randomly oriented ellipsoids, the particles orientation is averaged for all orientations.

**Polymeric Gaussian Coil**

\[
I(q) = \text{scale} I_0 P(q) + BKG
\]

\[
I_0 = \Phi_{\text{polymer}} V (\rho_{\text{polymer}} - \rho_{\text{solv}})^2
\]

\[
P(q) = \frac{2 \left[ (1 + UZ)^{-1/2} + Z - 1 \right]}{[(1 + U)Z^2]}
\]
\[ Z = \frac{(qR_g)^2}{(1 + 2U)} \]
\[ U = \left( \frac{M_w}{M_n} \right) - 1 \]
\[ V = \frac{M}{(N_A \delta)} \]

\( \Phi_{\text{polymer}} \), is the polymer volume fraction,

\( V \), is polymer coil’s volume,

\( M \), is the molecular weight of the polymer,

\( N_A \), is Avogardo’s number,

\( \delta \), is the polymer’s bulk density,

\( R_g \), is the polymer coil’s radius of gyration,

\( \rho_{\text{polymer}} \), and \( \rho_{\text{solvent}} \), are the scattering length densities of the polymer coil and solvent.
1.2.7 Cytotoxicity testing of triblock copolymers on HaCat cells at 10 mg/mL

HaCat cells were seeded at 10,000 cells per well and grown for 4 days in an incubator at 37 °C with 5 % CO₂. For each replicate there was a media blank, a positive control and a negative control. 50 µL of 20 mg/mL polymer solution was added to the cells in 50 µL of culture media to yield a tri-block copolymer concentration of 10 mg/mL. The dosed cells were stored in the incubator at 37 °C in 5 % CO₂ for 2 h until running the cytotoxicity assays.

For the LDH assay, 50 µL of cell supernatant was removed from each well and transferred to the wells on a black plate and 50 µL of assay solution was added to each well. The assay was covered by foil and left for 10 minutes, then immediately examined using a Promega Glomax Multi Detection System fluorescence plate reader with excitation wavelength of 560 nm and an emission wavelength of 590 nm. The data was then expressed as a percent cytotoxicity with reference to the cells which were dosed with 0.1 % (w/v) Triton-X (Equation 1).

\[
\text{Percent Cytotoxicity} = \frac{(\text{Dosed Cells} - \text{Background})}{(\text{Triton X Control} - \text{Background})} \times 100 \quad \text{(Equation 1)}
\]

After the LDH assay, the remaining HaCat cells in 50 µL of polymer in cell culture media (10 mg/mL) were then used for the MTS assay. The MTS assay solution (10 µL) was added to the remaining polymer in cell culture solution and HaCat cells and incubated at 37 °C with 5 % CO₂ for 2 h. The plates were then read using a fluorimeter at 490 nm. The data was expressed as percent metabolic activity compared to cells which were not dosed (Equation 2).

\[
\text{Percent Metabolic Activity} = \frac{(\text{Dosed Cells} - \text{Background})}{(\text{Healthy Cells} - \text{Background})} \times 100 \quad \text{(Equation 2)}
\]

1.2.8 Data handling and statistical analysis

Data is presented as the mean ± standard deviation of a minimum of three experiments. Statistical analysis was conducted on Prism (GraphPad, USA), with p < 0.05 considered statistically significant.
2. Results

**Figure S1.** $^1$H DOSY NMR spectra of a) the PEG 4 kDa macroinitiator and b) the PEG 10 kDa macroinitiator in CDCl$_3$ at 600 MHz. The peak at ca 3.6 ppm relates to the CH$_2$ of the PEG backbone, and the peak at ca 1.7 ppm is the CH$_3$ of the BiBB-modified end-groups.
Figure S2. $^1$H NMR of PNIPAM (blue), DMAMA (red), and DEGEMEMA (green) copolymers with structure and annotation inserted. Exemplar data for 10-10-10 A copolymers provided.
Figure S3. GPC traces of ABA copolymers synthesised by ATRP.
Figure S4: DOSY spectra confirm that protons associated with thermoresponsive “A” blocks (interpretation in figure 1) exhibit the same diffusion coefficient as PEG (CH$_2$, 3.7 ppm)

Figure S5. Frequency sweeps of DEGX-PX-DEGX copolymers (20 % w/v) at 25 (top) and 50 (bottom) °C. Architectures inserted.
**Figure S6.** Frequency sweeps of D10-P10-D10 (left) and N10-P10-N10 (right) copolymers (20% w/v) at 50°C. G’ is shown in black, G” is shown in red.
2.1 Effect of pH on thermoreversible gelation of PDMAEMA copolymers

PDMAEMA homopolymers exhibit pKas of approximately 7.5, depending on polymer molecular weight.\textsuperscript{[15]} Copolymers of PDMAEMA, however, have been shown to exhibit pKas as low as 6.1 depending on both copolymer and molecular weight.\textsuperscript{[16]} Thus, buffered solutions were used to maintain the pH above the pKa and hold the macromolecule in a predominantly unionised state. A single temperature ramp of the PDMAEMA triblock copolymers at 20 % w/v in pH 8.0 phosphate buffered solution was performed (Figure S7), which demonstrated comparable rheology to the copolymers in water.

![Figure S7: The rheograms of D10-P5-D10, D10-P10-D10, and D20-P10-D20 in phosphate buffers solution at pH 8. The rheograms show the change in G' (Blue) and G'' (Orange) with temperature](image-url)
Figure S8. Dynamic light scattering data demonstrating the increase in scattering from the polymer solutions with temperature. The darker colour correspond to the derived count rate.
Figure S9. Cytotoxicity of triblock copolymers relative to an untreated control as measured by metabolic activity (A) and membrane leakage (B), relative to untreated or triton-x treated cells, respectively. Cytotoxicity measured against HaCat cells dosed with PNIPAM (blue), PDMAEMA (red) and PDEGMEMA (green) at 10 mg/mL as identified by MTS (A) and LDH (B) assays, respectively. Results which are statistically different to healthy cells are denoted by *, **, *** where P values were greater than 0.05, 0.01 and 0.001 respectively relative to untreated cells. Data is presented as mean ± SD (n=4).
Table S2 Size, dispersity, and charge of block copolymers at 50 °C in aqueous solution (1 mg/mL) with G’ value at this temperature obtained from the temperature sweeps.

| Polymer ID                  | Dₜ (nm)  | PDI_DLS | ζ-potential (mV) |
|-----------------------------|----------|---------|------------------|
| PNIPAM₁₀-PEG₅-PNIPAM₁₀      | 171 ± 2  | 0.02 ± 0.01 | -26.7 ± 0.8     |
| PNIPAM₁₀-PEG₁₀-PNIPAM₁₀    | 87 ± 1   | 0.08 ± 0.01 | -12.4 ± 0.3     |
| PNIPAM₂₀-PEG₁₀-PNIPAM₂₀    | 207 ± 1  | 0.14 ± 0.01 | -31.7 ± 0.4     |
| PDMAEMA₁₀-PEG₅-PDMAEMA₁₀   | 168 ± 6  | 0.17 ± 0.02 | 19.5 ± 0.5      |
| PDMAEMA₁₀-PEG₁₀-PDMAEMA₁₀ | 44 ± 1   | 0.09 ± 0.02 | 10.8 ± 0.2      |
| PDMAEMA₂₀-PEG₁₀-PDMAEMA₂₀ | 76 ± 1   | 0.10 ± 0.01 | 14.2 ± 0.6      |
| PDEGMEMA₁₀-PEG₅-PDEGMEMA₁₀ | 188 ± 23 | 0.30 ± 0.07 | -23.6 ± 0.6     |
| PDEGMEMA₁₀-PEG₁₀-PDEGMEMA₁₀| 44 ± 1   | 0.14 ± 0.00 | -19.3 ± 1.4     |
| PDEGMEMA₂₀-PEG₁₀-PDEGMEMA₂₀| 44 ± 1   | 0.16 ± 0.01 | -14.3 ± 0.4     |
2.2 SANS parameters

Each series of ABA polymers were fitted against the models presented earlier. Results from the fits are presented below, each table compiling the data for an ABA copolymer type. The models used for the fits as abbreviated as follow:

PL_PGC = power law + polymeric Gaussian coils
Sp_PGC = polymeric Gaussian coils + sphere
Sp_PL = power law + sphere
Sp_HS_PGC = polymeric Gaussian coils + (sphere*hard sphere)
CSS_PL = power law + core-shell sphere
CSS_SHS_PGC = polymeric Gaussian coils + (core-shell sphere*sticky sphere)
Ep_Ep = ellipsoids + ellipsoids
Ep_HS_Ep = ellipsoids + (ellipsoids*hard sphere)
Cyl_PGC = polymeric Gaussian coils + cylinder
Cyl_SHS_PGC = polymeric Gaussian coils + (cylinder*sticky sphere)
CSCyl_HS_PGC = polymeric Gaussian coils + (core-shell cylinder*hard sphere)
EpCyl = elliptical cylinder
EpCyl_PL = power law + elliptical cylinder
EpCyl_HS = elliptical cylinder*hard sphere
FlexEpCyl = elliptical flexible cylinder
2.2 Fitting parameters from PNIPAM-\textit{b}-PEG-\textit{b}-PNIPAM series

**Table S3.** SANS fitting parameters for N20-P10-N20

| % (w/v) | 5   | 5   | 5   | 5   | 20  | 20  | 20  | 20  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Temp /°C| 25  | 37  | 40  | 50  | 25  | 37  | 40  | 50  |

| Model  | PL_PGC | CCS_PG_L | CCS_PG_C | CSS_PG_C | CSS_SHS_PG_C | CSS_SHS_PG_C | CSS_SHS_PG_C |
|--------|--------|-----------|-----------|-----------|--------------|--------------|--------------|
| Core (Å) |       | 205       | 205       | 230       | 195          | 193          | 225          |
| Shell (Å) | 115    | 92.0      | 91.74     | 64.87     | 69.3         | 62.6         |
| SLD_Core (x10$^{-6}$ Å$^{-2}$) |       | 4.37      | 4.13      | 2.72      | 3.35         | 3.12         | 3.47         |
| SLD_Shell (x10$^{-6}$ Å$^{-2}$) |       | 6.12      | 5.97      | 5.61      | 5.93         | 5.86         | 5.84         |
| Radius effect (Å) |   | 329       | 361       | 388       |
| Vol. Frac. Cor. | 0.35 | 0.33      | 0.22      |
| Stickiness |   | 0.89      | 0.47      | 0.46      |
| I$_0$ | 16.7  | 7.31      | 5.13      | 4.35      | 23.3         | 7.31         | 4.54         | 5.91         |
| Radius of Gyration (Å) | 41.5  | 19.7      | 14.8      | 12.6      | 19.0         | 19.4         | 12.6         | 15.3         |
| polydispersity | 1.88  | 1.88      | 1.88      | 1.88      | 1.88         | 1.88         | 1.88         | 1.88         |
| Poly_radius | 0.20  | 0.20      | 0.20      | 0.20      | 0.20         | 0.20         | 0.20         | 0.20         |
| Poly_thickness | 0.20  | 0.20      | 0.20      | 0.20      | 0.20         | 0.20         | 0.20         | 0.20         |
| Power law | 1.38  |           |           |           | 2.37         |               |               |
| A     | 0.001861 $^{4}$ | 0.21971 | 0.18636 | 0.073539 | 2.4822e-05  | 0.13005      | 0.25287      | 0.348         |
| B     | 0.047471 $^{3}$ | 0.020034 | 0.009044 | 0.004770 | 0.036886     | 0.053005     | 0.031864     | 0.016033      |
## Table S4. SANS fitting parameters for N10-P10-N10

| % (w/v) | 5   | 5   | 5   | 5   | 20  | 20  | 20  | 20  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Temp /°C|     |     |     |     |     |     |     |     |
|         | 25  | 37  | 40  | 50  | 25  | 37  | 40  | 50  |
| Model   | Sp_PG C | CSS_PG C | CSS_PG C | PL_PGC | CSS_SHS_PG C | CSS_SHS_PG C | CSS_SHS_PG C |
| Core (Å) | 220 | 168 | 161 | 153 | 146 | 156 |
| Shell (Å) | 75.0 | 68.9 | 68.0 | 62.33 | 57.9 |
| SLD_Core (x10^{-6} Å^{-2}) | 4.66 | 1.57 | 1.72 | 2.15 | 1.26 | 0.97 |
| SLD_Shell (x10^{-6} Å^{-2}) | 6.03 | 5.38 | 6.20 | 5.98 | 5.62 |
| Rad effective (Å) | 276 | 269 | 284 |
| Vol. Frac. Cor. | 0.25 | 0.34 | 0.40 |
| Stickiness | 0.47 | 0.24 | 0.12 |
| I0       | 20.8 | 10.8 | 11.4 | 10.8 | 27.6 | 15.0 | 11.1 | 5.70 |
| Radius of Gyration(Å) | 35.80 | 21.0 | 22.8 | 21.0 | 15.5 | 18.6 | 15.0 | 10.8 |
| polydispersity | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 |
| Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Poly_thickness | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Power law | 2.31 |     |     |     | 2.46 |     |     |     |
| A        | 2.8003e-05 | 0.03926 | 0.029711 | 0.044352 | 3.8178e-05 | 0.095286 | 0.095267 | 0.11491 |
| B        | 0.040768 | 0.03054 | 0.018813 | 0.013409 | 0.025283 | 0.044414 | 0.034318 | 0.032742 |
Table S5. SANS fitting parameters for N10-P5-N10

| % (w/v) | 5 | 5 | 5 | 5 | 20 | 20 | 20 | 20 |
| Temp /°C | 25 | 37 | 40 | 50 | 25 | 37 | 40 | 50 |

| Model     | PL_PGC | Cyl_PG | CSCyl_PGC | FlexEpCyl | PL_PGC | CSCyl_SHS_PGC | CSCyl_SHS_PGC | CSCyl_SHS_PGC |
|-----------|--------|--------|-----------|-----------|--------|---------------|---------------|---------------|
| Core (Å)  | 121    | 109    | 80.9      | 96.8      | 97.0   | 75.0          |               |               |
| Shell (Å) | 75.38  | 44.7   | 49.5      | 83.1      |        |               |               |               |
| SLD_Core (x10^{-6} Å^{-2}) | 3.94 | 1.63 | 4.40 | 2.96 | 2.75 | 1.92 |
| SLD_Shell (x10^{-6} Å^{-2}) | 5.88 | 6.08 | 5.76 | 5.06 |
| Length (Å) | 1431 | 15106 | 85528 | 426 | 504 | 12176 |
| Rad effective (Å) | 198 | 243 | 461 |
| Vol. Frac. Cor. | 0.18 | 0.26 | 0.24 |
| Stickiness | 1.65 | 1.48 | 1.09 |
| I0         | 13.3   | 6.00   | 2.57      | 12.5     | 12.4   | 9.79          | 2.37          |
| Radius of Gyr (Å) | 43.7 | 41.9 | 11.8 | 17.0 | 28.3 | 19.6 | 3.60 |
| polydispersity | 1.88 | 1.88 | 1.88 | 1.88 | 1.88 |
| Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 |
| Poly_thickness | 0.20 | 0.20 | 0.20 | 0.20 |
| Kuhn length (Å) | 89.5 |
| Axis ratio | 2.07 |
| Power law | 0.933 | 2.17 |
| A          | 0.00527 | 0.02044 | 0.039788 | 0.024185 | 2.4432e-05 | 0.15372 | 0.25366 | 0.27457 |
| B          | 0.07959 | 0.16405 | 0.028592 | 0.070252 | 0.14493 | 0.028961 | 0.0318 |
Additional comments on the fits of PNIPAM-\textit{b}-PEG-\textit{b}-PNIPAM series

The NIPAM ABA series, of the three studied, was the ABA which produced micelles with more distinctive core/shell segregation, as shown by the suitability of the core-shell model fittings. We observe a relatively “wet” (hydrated) core and shell. A SLD around $6 \times 10^{-6} \, \text{Å}^{-2}$ corresponds to a shell comprising 95 wt% D$_2$O and a SLD around $3 \times 10^{-6} \, \text{Å}^{-2}$ corresponds to a core formed by 20 wt% D$_2$O. The temperature dependence, when present, was weak but indicated a reduction of D$_2$O penetration both in the shell and core, i.e., lower values of SLD, in line with a temperature-induced desolvation.

The radii of the micellar aggregates showed a weak sensitivity to temperature. For instance, the total radius for N10P10N10 (5 wt\%) changed from 220 Å to 230 Å, from 37 to 50°C, respectively. At 20wt \%, a decrease of 14 Å was observed, from 228 to 214 Å. The total values of the radius observed at 20 wt\% are generally smaller than at 5 wt\%.

The particle “stickiness”, extracted from the S(q) when available, was the more sensitive parameter, with more sticky particles as temperature increases, while the correlated volume fraction showed low sensitivity.

In summary, the largest differences were observed below and above the transition temperature, i.e., from 25 to 37°C. Above 37°C, the micellar aggregates seem to have fully formed and do not undergo major morphology changes.
## Fitting parameters from PDEGMEMA-b-PEG-b-PDEGMEMA

### Table S6. SANS fitting parameters for DEG20-P10-DEG20

| % (w/v) | 5   | 5   | 5   | 5   | 20  | 20  | 20  | 20  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Temp ˚C | 25  | 37  | 40  | 50  | 25  | 37  | 40  | 50  |

| Model       | EpEp | CSS_SHS_PG C | CSS_SHS_PGC | CSS_SHS_PGC | Ep_HS_pEp | CSS_SHS_PGC | CSS_SHS_PGC | CSS_SHS_PGC |
|-------------|------|--------------|--------------|--------------|-----------|--------------|--------------|--------------|
| Core (Å)    |      | 115          | 116          | 115          |           | 111          | 117          | 113          |
| Shell (Å)   |      | 67.3         | 58.0         | 45.5         |           | 48.5         | 43.1         | 44.9         |
| SLD_Core (x10^{-6} Å^{-2}) | 4.73 | 5.64 | 5.66 | 3.83 | 3.91 | 4.45 | 4.41 |
| SLD_Shell (x10^{-6} Å^{-2}) | 6.28 | 6.27 | 6.25 | 6.23 | 6.21 | 6.14 |
| Rad effective (Å) | 222  | 224  | 393 | 86.7 | 171 | 182 | 179.8 |
| Vol. Frac. Cor. | 0.08 | 0.07 | 0.06 | 0.13 | 0.33 | 0.35 | 0.32 |
| Stickiness  | 15.9 | 64.8 | 1.33 | 1.65 | 0.89 | 0.14 |        |
| I0          | 62.3 | 61.2 | 55.5 | 61.7 | 72.0 | 51.2 |        |
| Radius of Gyration (Å) | 15.24 | 15.1 | 14.1 | 15.0 | 16.6 | 13.3 |        |
| polydispersity | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 |
| Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Poly_thickness | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Radius polar 1 (Å) | 9.67 |      |      |      | 9.24 |      |      |      |
| Radius equatorial 1 (Å) | 37.7 |      |      |      | 68.7 |      |      |      |
| Radius polar 2 (Å) | 10.2 |      |      |      | 6.05 |      |      |      |
| Radius equatorial 2(Å) | 375 |      |      |      | 690 |      |      |      |
| A           | 0.209 | 4.3307 | 3.8876 | 3.8084 | 0.32989 | 1.1036 | 1.6902 | 2.0743 |
|   | 4  | 0.0257 | 0.00282 | 0.00198 | 0.00091 | 0.00263 | 0.00913 | 0.00712 | 0.00430 |
|---|----|--------|---------|---------|---------|---------|---------|---------|---------|
| B |    |        |         |         |         |         |         |         |         |
Table S7. SANS fitting parameters for DEG10-P10-DEG10

| % (w/v) | Temp /°C | Model | Ep_PL | Ep_SHS_P CG | Ep_SHS_P CG | Ep_SHS_P CG | Ep_HSp Ep | Ep_SHS_P CG | Ep_SHS_P CG | Ep_SHS_P CG |
|---------|----------|-------|-------|------------|------------|------------|------------|------------|------------|------------|------------|
| 5       | 25       | Polar radius (Å) | 8.69 | 124 | 135 | 105.5 | 6.85 | 87.5 | 87.0 | 82.5 |
| 5       | 37       | Equatorial radius (Å) | 27.1 | 64.73 | 69.2 | 78.6 | 31.4 | 59.1 | 65.1 | 86.6 |
| 5       | 40       | SLD particle (x10⁻⁶ Å⁻²) | 4.81 | 3.99 | 3.18 | 2.90 | 3.83 | 3.61 | 3.56 | 3.64 |
| 5       | 50       | Rad effective (Å) | 182 | 161 | 185 | 63.9 | 106 | 113 | 139 |
| 5       | 25       | Vol. Frac. Cor. | 0.05 | 0.07 | 0.09 | 0.12 | 0.27 | 0.28 | 0.37 |
| 5       | 37       | Stickiness | 0.40 | 0.68 | 0.93 | 1.23 | 1.83 | 0.68 |
| 5       | 40       | I₀ | 33.9 | 26.6 | 9.66 | 41.7 | 30.6 | 12.2 |
| 5       | 50       | Radius of Gyration (Å) | 32.1 | 28.1 | 10.07 | 35.8 | 29.7 | 17.6 |
| 20      | 25       | polydispersity | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 |
| 20      | 37       | Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| 20      | 40       | Poly_thickness | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| 20      | 50       | Power law | 1.70 | 0.037186 | 0.027845 | 0.045392 | 0.28058 | 0.13216 | 0.1496 | 0.21493 |
| A       | 0.1875   | 0.037186 | 0.027845 | 0.045392 | 0.28058 | 0.13216 | 0.1496 | 0.21493 |
| B       | 0.00054 | 0.038567 | 0.03047 | 0.011662 | 0.28972 | 0.091413 | 0.071448 | 0.045757 |
Table S8. SANS fitting parameters for DEG10-P5-DEG10

| % (w/v) | 5 | 5 | 5 | 5 | 20 | 20 | 20 | 20 |
|---------|---|---|---|---|----|----|----|----|
| Temp /°C | 25 | 37 | 40 | 50 | 25 | 37 | 40 | 50 |

| Model | EpCyl | Cyl_PG | Cyl_PG | Cyl_PGC | EpCyl_HS_p | Ep_SHS_P_L | Cyl_SHS_PG_C | Cyl_SHS_PG_C |
|-------|-------|--------|--------|---------|------------|-------------|---------------|---------------|
| Radius (Å) | 70.8 | 70.3 | 70.4 | 58.5 | 63.0 | 71.1 |
| SLD particle (x10^{-6} Å^2) | 5.83 | 6.02 | 6.02 | 6.01 | 5.02 | 5.95 | 5.97 | 5.69 |
| Rad effective (Å) | | | | | | | 113 | 118 | 115 |
| Vol. Frac. Cor. | | | | | | 0.28 | 0.30 | 0.38 |
| Stickiness | | | | | | 0.48 | 0.44 | 1.43 |
| I_0 | 28.4 | 28.4 | 12.9 | 33.9 | 24.1 | 7.57 |
| Radius of Gyration (Å) | 24.6 | 24.6 | 14.72 | 26.7 | 22.1 | 5.00 |
| polydispersity | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 | 1.10 |
| Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| radius pol (Å) | 8.86 | | | | 7.74 |
| axis ratio | 2.4 | | | | 3.1 |
| Length (Å) | 171 | 1091 | 1401 | 12000 | 315 | | | 787. | 563 |
| A | 1.823 | 3.3445 | 3.4752 | 3.6071 | 8.2422 | 14.819 | 18.267 | 6.2593 |
| B | 0.012522 | 0.008532 | 0.002682 | 0.051994 | 0.034355 | 0.01396 |
Additional comments on the fits of PDEGMEMA-b-PEG-b-PDEGMEMA series

The DEG ABA series showed less well-defined micellar aggregates, as the core and shell were not fully resolved in the DEG10-P10-DEG10 construct. For DEG20-P10-DEG20, a wetter core was observed, with SLD values suggesting a core formed of 87 wt% D₂O at 5 wt% and 67 % at 20 wt% ABA. The data for DEG10-P10-DEG10 could not be fitted by a core-shell model, suggesting that difference in hydration between the core and the shell was too small to be resolved. This could either be due a small difference in polarity between PEG and PDEG or geometric constrains imposed to the ABA conformation due to differences between PEG and PDEG. The predicted log Ps for PEG and PDEG are 0.38 and -6.5 at 25°C, respectively, which shows that PDEG is more hydrophobic than PEG at 25°C. Therefore, PDEG is also significantly more hydrophobic than PNIPAM, both would suggest that PDEG-PEG-PDEG micelles are even more segregated than PNIPAM-PEG-PNIPAM due to the larger differences in hydrophobicity. The fact that we do not observe segregation at all for DEG10-P10-DEG10 and some segregation with higher levels of hydration for DEG20-P10-DEG20, where larger blocks of DEG are present, suggests a geometric or steric reason for the wetter micelles. Curiously, DEG10-P10-DEG10 data are better fitted with ellipsoids, not spheres. Either the polymeric aggregates show a broader size polydispersity, which often results in either polydisperse spheres or ellipsoids being suitable models, or the DEG imposes such steric constraints that the micelles cannot form spherical objects.

At 25°C, the SANS data were fitted using ellipsoids, instead of polymeric Gaussian coils as was done for PNIPAM-PEG-PNIPAM. This shows that at 25°C supramolecular aggregates are already present, which could be due the higher hydrophobicity of DEG.
### Fitting parameters from PDMAMA-b-PEG-b-PDMAMA

#### Table S9. SANS fitting parameters for D20-P10-D20

| % (w/v) | 5          | 5          | 5          | 5          | 20         | 20         | 20         | 20         |
|---------|------------|------------|------------|------------|------------|------------|------------|------------|
| Temp /°C| 25         | 37         | 40         | 50         | 25         | 37         | 40         | 50         |
| Model   | EpCyl      | Sp_HSp_PG C | Sp_HSp_PG C | Sp_HSp_PG C | EpCyl_P L  | Sp_SHS_PG C | Sp_SHS_PG C | Sp_SHS_PG C |
| Radius (Å) | 108       | 112        | 125        | 76.5       | 84.3       | 111        |            |            |
| SLD particle (x10^{-6} Å^2) | 4.11  | 5.23       | 4.99       | 4.73       | 4.83       | 5.17       | 5.13       | 4.17       |
| Rad effective (Å) | 215      | 203        | 197        | 144        | 154        | 171.9      |            |            |
| Vol. Frac. Cor. | 0.04     | 0.05       | 0.07       | 0.21       | 0.27       | 0.35       |            |            |
| Stickiness |          |            |            | 0.64       | 0.54       | 0.75       |            |            |
| I₀      | 28.5      | 34.07      | 11.4       | 12.9       | 12.9       | 12.9       |            |            |
| Radius of Gyration (Å) | 36.2     | 39.90      | 21.2       | 23.1       | 23.1       | 23.1       |            |            |
| polydispersity | 1.24     | 1.24       | 1.24       | 1.24       | 1.24       | 1.24       |            |            |
| Poly_radius | 0.20      | 0.20       | 0.20       | 0.20       | 0.20       | 0.20       |            |            |
| Poly_thickness |          |            |            |            |            |            |            |            |
| Radius minor (Å) | 7.68     | 5.17       |            |            |            |            |            |            |
| Axis ratio | 3.6       | 9.2        |            |            |            |            |            |            |
| Length (Å) | 382      | 115        |            |            |            |            |            |            |
| Power law | 3.13      |            |            |            |            |            |            |            |
| A        | 0.1396    | 0.23851    | 0.20209    | 0.22029    | 1.1203     | 0.20935    | 0.82071    | 0.41531    |
| B        | 0.068768  | 0.056535   | 0.02701    | 2.7878e-07 | 0.18399    | 0.16578    | 0.093177   |            |
Table S10. SANS fitting parameters for D10-P10-D10

| % (w/v) | 5   | 5   | 5   | 5   | 20  | 20  | 20  | 20  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|
| Temp /°C | 25  | 37  | 40  | 50  | 25  | 37  | 40  | 50  |
| Radius (Å) | 7.13 | 121 | 124.2 | 127 | 5.64 | 103 | 109 | 119 |
| SLD_particle (x10^{-6} Å^{-2}) | 4.50 | 5.86 | 5.85 | 5.80 | 3.53 | 5.78 | 5.69 | 5.62 |
| Rad effective (Å) | 256 | 256 | 181 | 158 | 161 | 181 |
| Vol. Frac. Cor. | 0.06 | 0.06 | 0.02 | 0.22 | 0.25 | 0.32 |
| Stickiness | 0.77 | 0.80 | 0.65 | 1.22 | 1.41 | 0.53 |
| I_0 | 34.6 | 24.5 | 13.7 | 65.0 | 59.4 | 24.6 |
| Radius of Gyration (Å) | 27.6 | 22.5 | 12.0 | 36.0 | 21.4 | 12.4 |
| Polydispersity | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 | 1.20 |
| Poly_radius | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 | 0.20 |
| Poly_thickness | | | | | | |
| axis ratio | 19.1 | | | | 16.2 | | |
| Kuhn length (Å) | 1423 | | | | 111 | | |
| Length (Å) | 572 | | | | 376 | | |
| A | 0.008254 | 1.3363 | 1.4666 | 1.6821 | 0.018187 | 3.8977 | 3.4976 | 4.347 |
| B | 0.022129 | 0.018615 | 0.0072293 | | 0.071311 | 0.028181 | 0.018729 |
Table S11. SANS fitting parameters for D10-P5-D10

| % (w/v) | Temp /°C | 5   | 5   | 5   | 5   |
|---------|----------|-----|-----|-----|-----|
|         | 25       | 37  | 40  | 50  |     |

|               | Cyl_PGC  | Cyl_PGC | Cyl_PGC | Cyl_PGC |
|---------------|----------|----------|----------|----------|
| Radius (Å)    | 84.1     | 92.5     | 95.3     | 99.6     |
| length (Å)    | 1008     | 739      | 738.8    | 1052     |
| SLD particle  | 4.82     | 4.60     | 4.62     | 4.57     |
| (x10⁻⁶ Å⁻²)   |          |          |          |          |
| I₀            | 40.4     | 13.8     | 12.5     | 8.48     |
| Radius of     | 26.3     | 10.8     | 7.42     | 4.02     |
| Gyration (Å)  |          |          |          |          |
| polydispersity| 1.10     | 1.10     | 1.10     |          |
| Poly_radius   | 0.20     | 0.20     | 0.20     |          |
| A             | 0.10316  | 0.10634  | 0.11024  | 0.11736  |
| B             | 0.01186  | 0.0045328| 0.0039007| 0.0023821|
Additional comments on the fits of PDMAMA-b-PEG-b-PDMAMA series

The SANS data analysis for the PDMAMA ABA series showed no observable segregation between the core and shell of the micellar aggregates. For PNIPAM-PEG-PNIPAM, core-shell structures were observed for both A20-B10-A20 and A10-B10-A10 architectures. For PDEG-PEG-PDEG, core-shell structures were only observed for the A20-B1-A20 architecture. As discussed previously, this lack of observable segregation could be due to a reduced difference of hydrophobicity between the copolymers. The predicted Log P at 25°C for PDMAMA is 0.67, which lies between PNIPAM and PDEG, and is far larger than PEG. This would suggest that PDMAMA should be the intermediate case. Therefore, this lack of segregation cannot be due only to differences in hydrophobicity of the copolymers. In a similar way to PDEG, the data from PDMAMA systems required a S(q) at 5 wt% and were fitted as discrete objects at 25°C, instead of polymeric Guassian coils. Unlike PDEG, PDMAMA systems form spheres instead of ellipsoids. While it does not explain the lack of core-shell structures, it seems that a high level of hydrophobicity, high enough to lead to the formation of supramolecular aggregates below the transition temperature is a common feature. A significant contributor to this could be the dependence of LCST on Mn in DMAMA,\textsuperscript{[17]} such that higher Mn chains in the polydisperse sample transition even at the lowest temperatures studied.\textsuperscript{[17]}
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