Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for:

RAFT dispersion polymerization of lauryl methacrylate in ethanol-water binary mixtures: synthesis of diblock copolymer vesicles with deformable membranes

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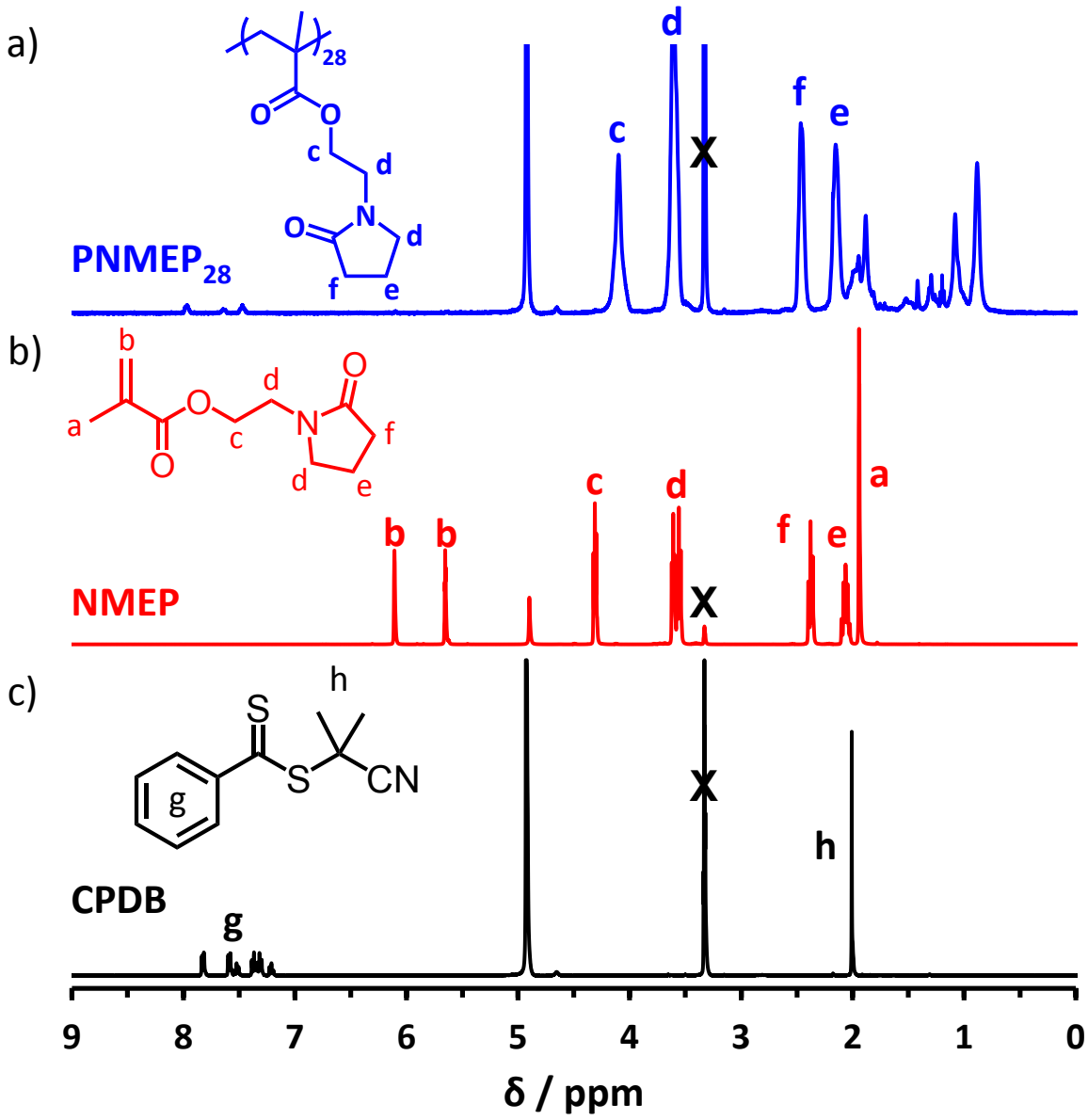

Figure S1. ^{1}H NMR spectra recorded in d_4-methanol for (a) $PNMEP_{28}$ macro-CTA, (b) NMEP monomer and (c) CPDB RAFT agent.

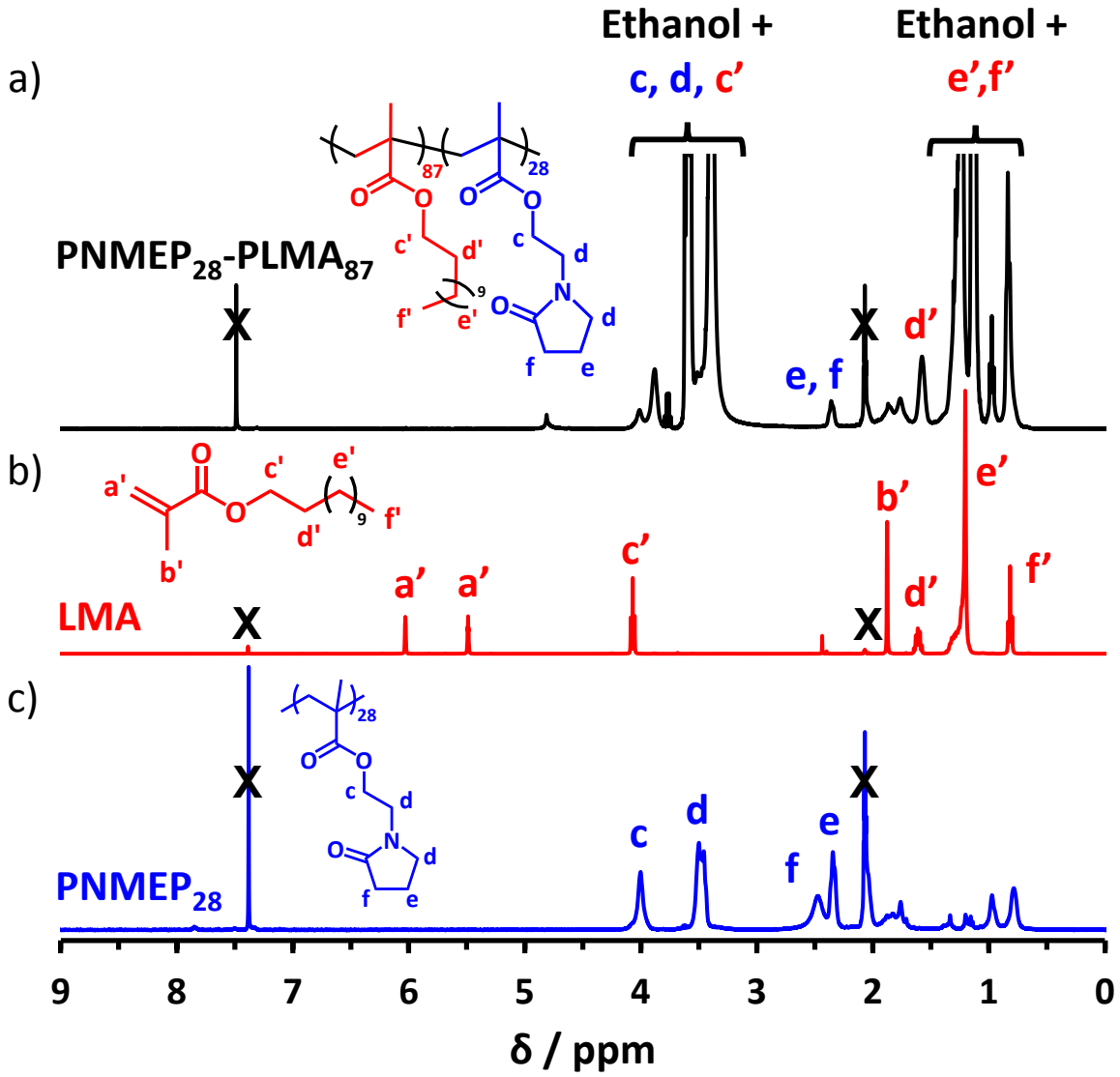

Figure S2. ^{1}H NMR spectra recorded in a 10:1 d_1-chloroform:d_6-acetone solvent mixture for (a) $PNMEP_{28}$-$PLMA_{87}$ diblock copolymer, (b) LMA monomer and (c) $PNMEP_{28}$ macro-CTA.

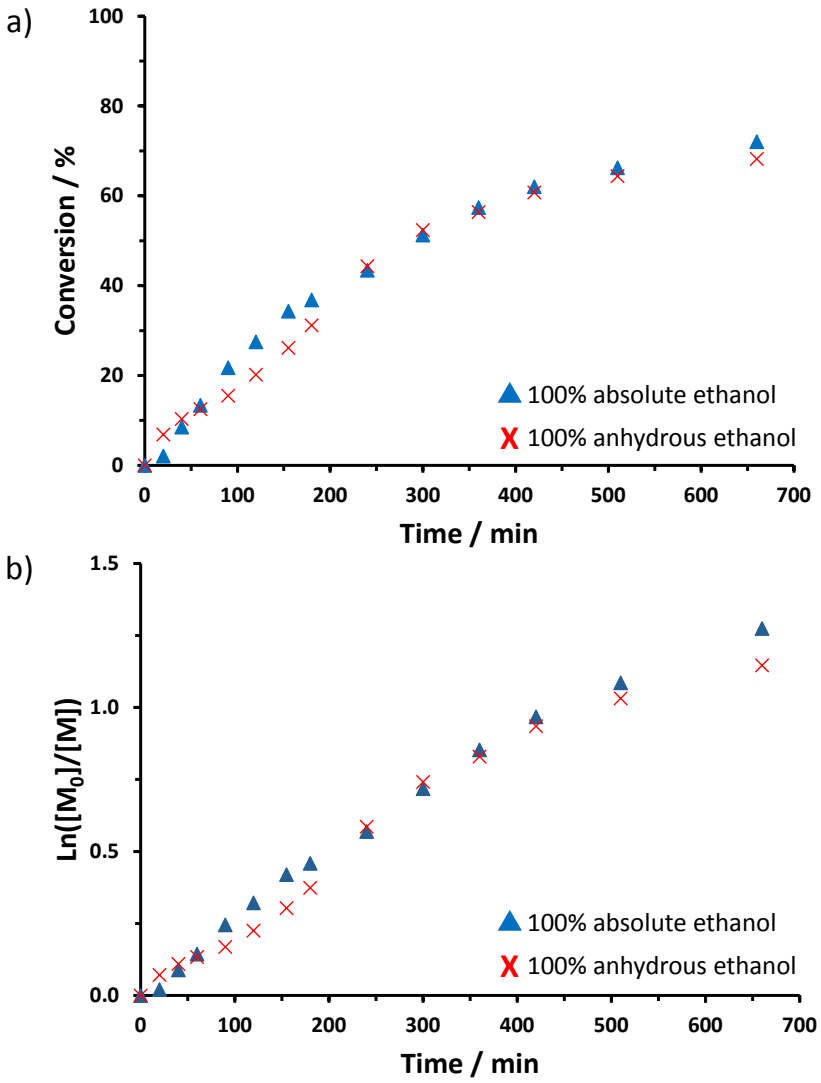

Figure S3. Conversion vs. time curves obtained by ^{1}H NMR spectroscopy studies of the RAFT dispersion polymerization of LMA at 70 °C using a $PNMEP_{28}$ macro-CTA and ACVA initiator ([$PNMEP_{28}$]/[ACVA] molar ratio = 5.0) at 20% w/w solids using either laboratory-grade ethanol or anhydrous ethanol. (b) Corresponding semi-logarithmic plots calculated for the same kinetic data.

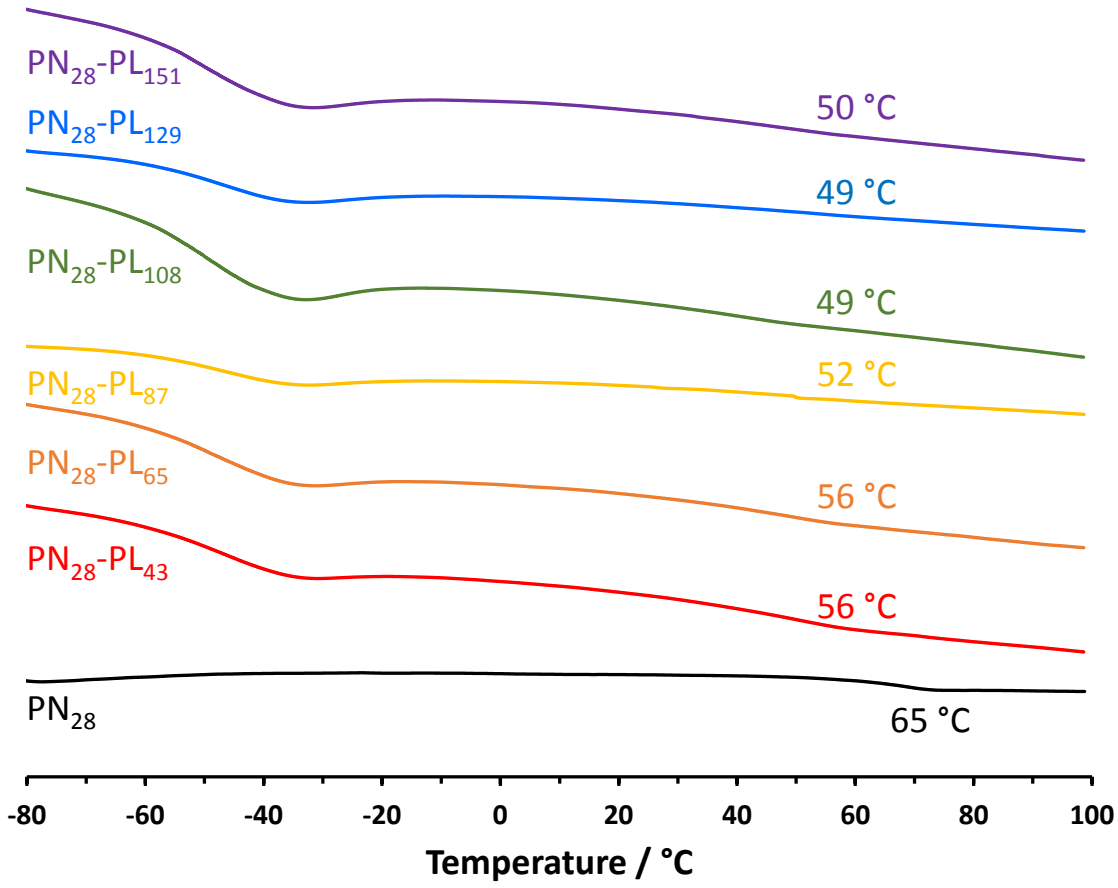

Figure S4. Differential scanning calorimetry (DSC) traces obtained for the $PNMEP_{28}$ macro-CTA precursor and a series of $PNMEP_{28}$-$PLMA_x$ diblock copolymers using a heating rate of 10 °C min^{-1}

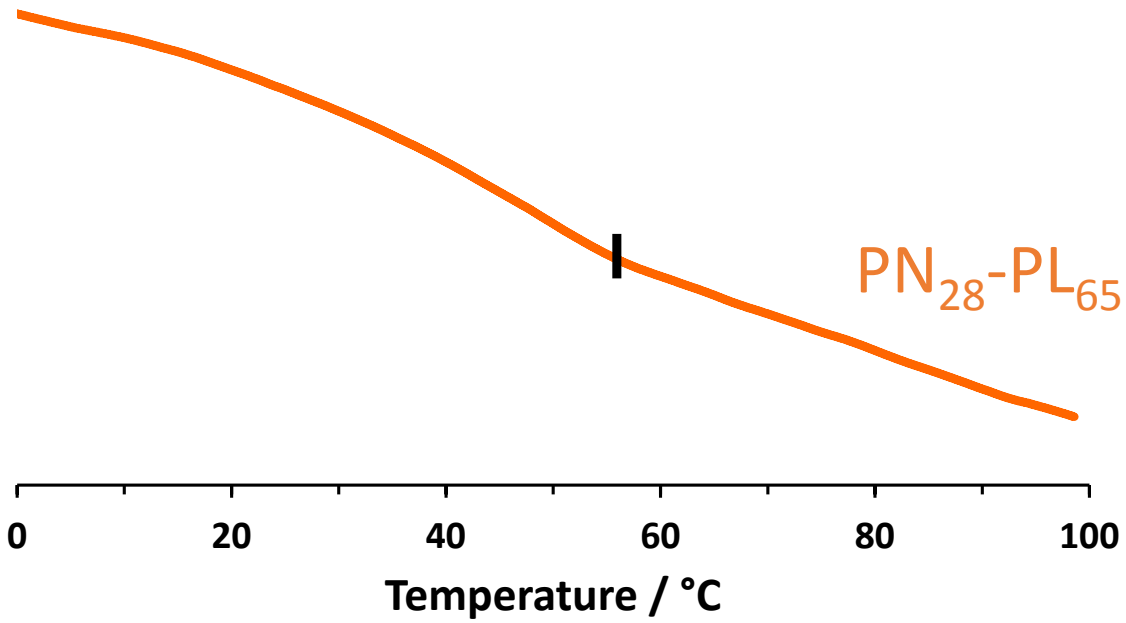

Figure S5. Magnified DSC thermogram of $PNMEP_{28}$-$PLMA_{65}$ with the T_g indicated at 56 °C.

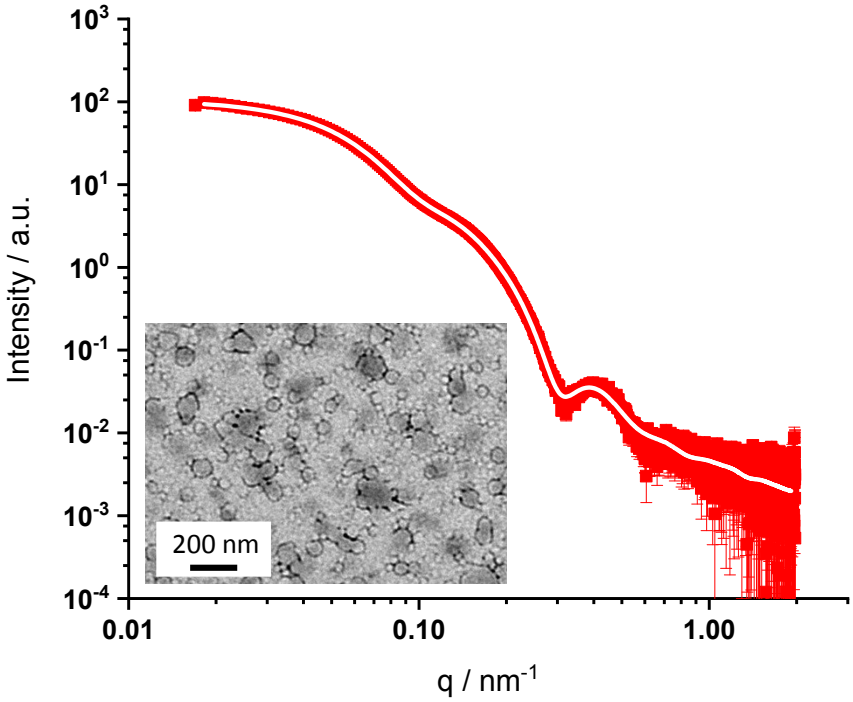

Figure S6. SAXS pattern recorded for a 1.0% w/w copolymer dispersion of $PNMEP_{28}$-$PLMA_{43}$ in 80:20 w/w ethanol-water at 20 °C. The white line indicates the data fit obtained a spherical plus vesicle two-population model. Inset is a TEM image of the $PNMEP_{28}$-$PLMA_{43}$ diblock copolymer nanoparticles indicating the presence of small spheres and larger vesicles.

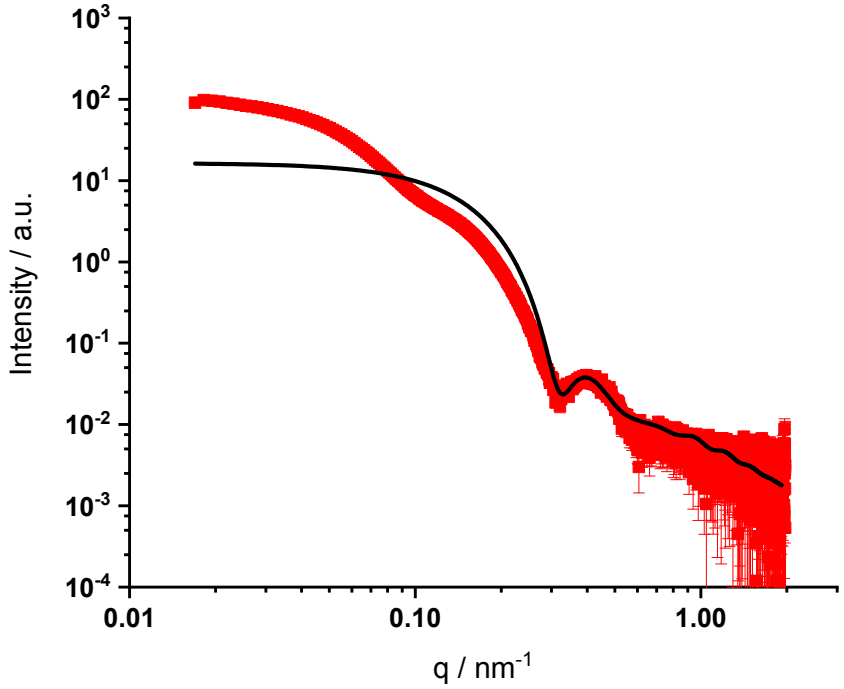

Figure S7. SAXS pattern recorded for a 1.0% w/w dispersion of $PNMEP_{28}$-$PLMA_{43}$ nano-objects in 80:20 w/w ethanol-water prepared at 20% w/w solids concentration. The black solid line indicated the unsatisfactory data fit obtained when attempting to incorrectly use a spherical micelle model.

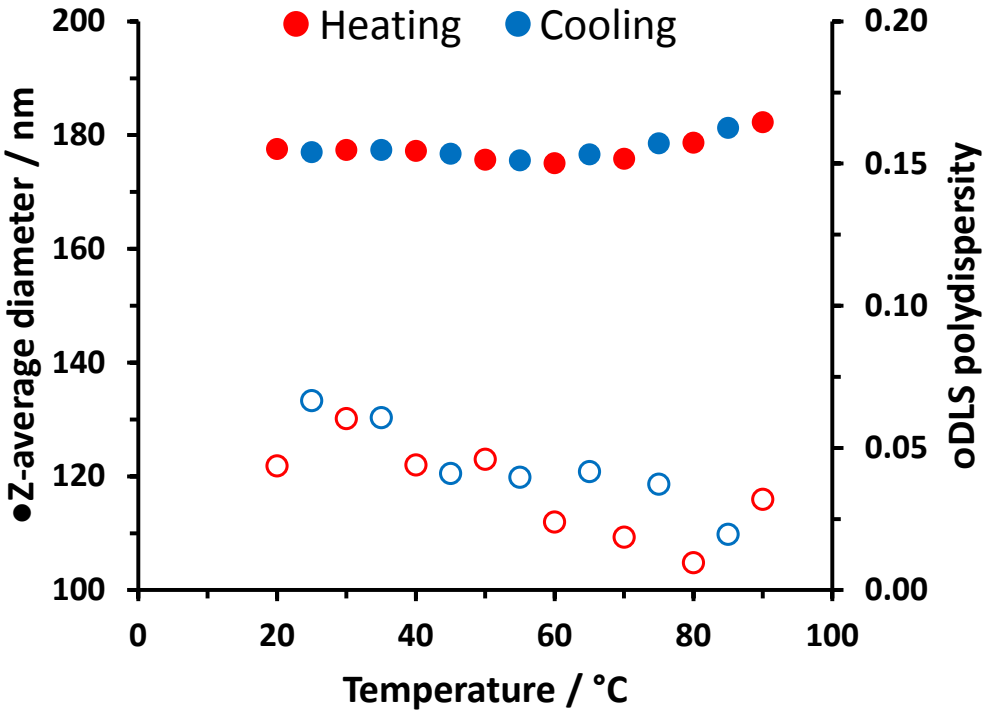

Figure S8. Z-average diameter obtained by DLS studies of a 0.1% w/w aqueous dispersion of $PNMEP_{28}$-$PLMA_{87}$ nanoparticles synthesized in an 80:20 w/w ethanol-water mixture on heating from 20 to 90 °C and the corresponding data on cooling from 90 to 25 °C. The z-average diameter and DLS polydispersity remains essentially constant over the entire temperature range, indicating an unexpected lack of thermoresponsive behavior.

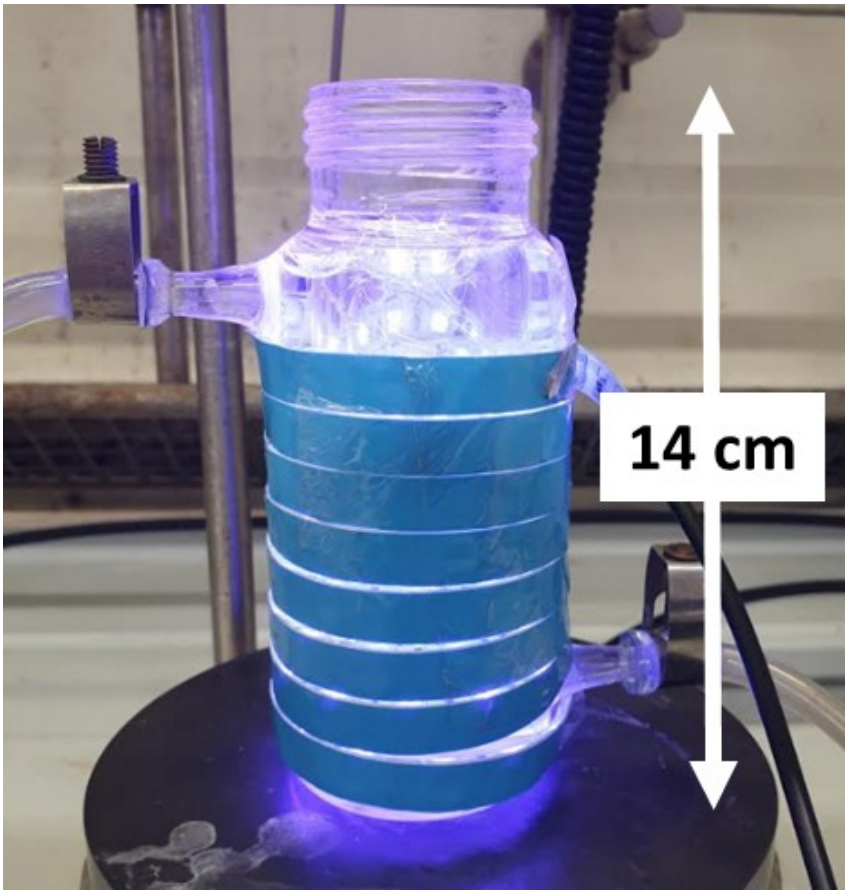

Figure S9. Digital photograph of the LED photoreactor used for removal of RAFT end-groups. The reactor consists of a water-jacketed Schlenk tube wrapped in blue LED light strips (λ = 405 nm, 0.37 mW cm^{-2}).

Figure S10. Digital photographs recorded for a 7.5% w/w aqueous dispersion of $PNMEP_{28}$-$PLMA_{87}$ vesicles recorded before (upper) and after (lower) exposure to blue LED light for 3 h at 50 °C. UV GPC studies confirm that this protocol is sufficient to remove almost all of the dithibenzoate end-groups, which is consistent with the observed loss in color.

SAXS model

In general, the intensity of X-rays scattered by a dispersion of nano-objects [usually represented by the scattering cross section per unit sample volume, $\frac{d\Sigma}{d\Omega}(q)$] can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = NS(q)\int_0^\infty \dots \int_0^\infty F(q,r_1,\dots,r_k)^2 \Psi(r_1,\dots,r_k) dr_1 \dots dr_k \quad \text{S1}$$

where $F(q, r_1, \dots, r_k)$ is the form factor, $r_1, \dots, r_k$ is a set of *k* parameters describing the structural morphology, $\Psi(r_1, \dots, r_k)$ is the distribution function, S(q) is the structure factor and *N* is the nano-object number density per unit volume expressed as:

$$N = \frac{\varphi}{\int_0^\infty \dots \int_0^\infty V(r_1,\dots,r_k)\Psi(r_1,\dots,r_k) dr_1 \dots dr_k} \quad \text{S2}$$

where $V(r_1, \dots, r_k)$ is volume of the nano-object and φ is their volume fraction in the dispersion. For all SAXS experiments conducted herein, a dilute copolymer concentration of 1.0 % w/w was utilised. As such, for all analysis and modelling it was assumed that s(q) = 1.

Vesicle model[1]

The vesicle form factor in Equation (S1) is expressed as:

$$F_{ves}(q) = N_v^2 \beta_m^2 A_m^2(q) + N_v \beta_{vc}^2 F_c(q,R_g) + N_v(N_v - 1)\beta_{vc}^2 A_{vc}^2(q) + 2N_v^2 \beta_m \beta_{vc} A_m(q) A_{vc}(q) \quad \text{S3}$$

The X-ray scattering length contrast for the membrane-forming block (PLMA) and the coronal stabilizer block (PNMEP) is given by $\beta_m = V_m(\xi_m - \xi_{sol})$ and $\beta_{vc} = V_{vc}(\xi_{vc} - \xi_{sol})$, respectively, where ξ_m, ξ_{vc} and ξ_{sol} are the X-ray scattering length densities of the membrane-forming block ($\xi_{PLMA} = 8.81 \times 10^{10}$ cm^{-2}), the coronal stabilizer block ($\xi_{PNMEP} = 11.6 \times 10^{10}$ cm^{-2}) and the solvent ($\xi_{sol} = 7.859 \times 10^{10}$ cm^{-2}). V_m and V_{vc} are the volumes of the membrane-forming block and the coronal stabilizer block, respectively. Using the molecular weights of the PLMA and PNMEP blocks and their respective mass densities ($\rho_{PLMA} = 0.93$ g cm^{-3} and $\rho_{PNMEP} = 1.272$ g cm^{-3}), the individual block volumes can be calculated from $V = \frac{M_{n,pol}}{N_A \rho}$, where $M_{n,pol}$ corresponds to the number-average molecular weight of the block determined by ^{1}H NMR spectroscopy. The amplitude of the membrane self-term is:

$$A_m(q) = \frac{V_{out}\varphi(qR_{out}) - V_{in}\varphi(qR_{in})}{V_{out} - V_{in}} e^{\left(-\frac{q^2\sigma_{in}^2}{2}\right)} \quad \text{S4}$$

where $R_{in} = R_m - \frac{1}{2}T_m$ is the inner radius of the membrane, $R_{out} = R_m + \frac{1}{2}T_m$ is the outer radius of the membrane, $V_{in} = \frac{4}{3}\pi R_{in}^3$, $V_{out} = \frac{4}{3}\pi R_{out}^3$. It should be noted that Equation S4 differs from that reported in the original work. More specifically, the exponent term in Equation S4 represents a sigmoidal interface between the blocks, with a width σ_{in} accounting for a decaying scattering length density at the membrane surface. The numerical value of σ_{in} was fixed at 2.2. The mean vesicle aggregation number, N_v, is given by:

$$N_v = (1 - x_{sol})\frac{V_{out} - V_{in}}{V_m} \qquad \text{S5}$$

where x_{sol} is the solvent (i.e. 80:20 ethanol-water) volume fraction within the vesicle membrane. A simpler expression for the corona self-term of the vesicle model than that used for the spherical micelle corona self-term was preferred because the contribution to the scattering intensity from the corona block is much less than that from the membrane block in this case. Assuming that there is no penetration of the solvophilic coronal blocks into the solvophobic membrane, the amplitude of the vesicle corona self-term is expressed as:

$$A_{vc}(q) = \Psi(qR_g)\frac{1}{2}\left[\frac{sin\left[q(R_{out} + R_g)\right]}{q(R_{out} + R_g)} + \frac{sin\left[q(R_{in} - R_g)\right]}{q(R_{in} - R_g)}\right] \qquad \text{S6}$$

where the term outside the square brackets is the factor amplitude of the corona block copolymer chain such that:

$$\Psi(qR_g) = \frac{1 - exp^{(-qR_g)}}{(qR_g)^2} \qquad \text{S7}$$

The average experimental R_g value of 2.3 nm for the $PNMEP_{28}$ coronal block is higher than the estimated value. The latter can be calculated from the total contour length of the $PNMEP_{28}$ block, $L_{PNMEP28} = 28 \times 0.255$ nm = 7.14 nm (since the projected contour length per NMEP monomer repeat unit is defined by two C-C bonds adopting an *all-trans* conformation, 0.255 nm) and the Kuhn length of 1.53 nm based on the known literature value for poly(methyl methacrylate) result in an approximate R_g of $(7.14 \times 1.53/6)^{0.5} = 1.35$ nm.

For the vesicle model, it was assumed that two parameters are polydisperse: the overall radius of the vesicles and the membrane thickness (R_m and T_m, respectively). Each is assumed to have a Gaussian distribution, so the polydispersity function in Equation (S1) can be expressed as:

$$\Psi(r_1,r_2) = \frac{1}{\sqrt{2\pi\sigma_{R_m}^2}}exp\left(-\frac{(r_1 - R_m)^2}{2\sigma_{R_m}^2}\right)\frac{1}{\sqrt{2\pi\sigma_{T_m}^2}}exp\left(-\frac{(r_1 - T_m)^2}{2\sigma_{T_m}^2}\right) \qquad \text{S8}$$

where σ_{Rm} and σ_{Tm} are the standard deviations for R_m and T_m, respectively. Following Equation S2, the number density per unit volume for the vesicle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty \int_0^\infty V(r_1,r_2)\Psi(r_1,r_2)dr_1dr_2} \qquad \text{S9}$$

where φ is the total volume fraction of copolymer in the vesicles and $V(r_1, r_2)$ is the total volume of copolymers in a vesicle [$V(r_1, r_2) = (V_m + V_{vc})N_v(r_1, r_2)$]. Programming tools within the Irena SAS Igor Pro macros were used to implement the scattering models.

Additionally, a Gaussian peak $\left(Aexp\left[-\left(\frac{q-q_{peak}}{width}\right)^2\right]\right)$ was added to the vesicle model in order to account for the subtle feature observed at q ~ 0.1 nm^{-1} for the 1.0 % w/w dispersions of PNMEP$_{28}$-PLMA$_{129}$ and PNMEP$_{28}$-PLMA$_{151}$ at 20 °C (Figure 5). Thus, the entire scattering pattern would be described as:

$$I(q) = \frac{d\Sigma}{d\Omega}(q) + Bq^{-p} + Aexp\left[-\left(\frac{q-q_{peak}}{width}\right)^2\right] \quad \text{S10}$$

where the first term represents scattering from spherical micelles (Equations S1 and S2).

Spherical model

The spherical micelle form factor equation for Equation S1 is given by[2]:

$$F_{sph}(q) = N_s^2\beta_s^2A_s^2(q,R_s) + N_s\beta_c^2F_c(q,R_g) + (q) \quad \text{S11}$$

Where R_s is the core radius of the spherical micelle, R_g, is the radius of gyration of the PNMEP corona block. The core block and the corona block X-ray scattering length contrast is given by $\beta_s = V_s(\xi_s - \xi_{sol})$ and $\beta_s = V_c(\xi_c - \xi_{sol})$, respectively. Here ξ_s, ξ_c and ξ_{sol} are the X-ray scattering length densities of the core-forming block (ξ_{PLMA} = 8.81 × 10^{10} cm^{-2}), the coronal stabilizer block (ξ_{PNMEP} = 11.6 × 10^{10} cm^{-2}) and the solvent (ξ_{sol} = 7.859 × 10^{10} cm^{-2}). V_s and V_c are the volumes of the core-forming block and the coronal stabilizer block, respectively. Using the molecular weights of the PLMA and PNMEP blocks and their respective mass densities (ρ_{PLMA} = 0.93 g cm^{-3} and ρ_{PNMEP} = 1.272 g cm^{-3}), the individual block volumes can be calculated from $V = \frac{M_{n,pol}}{N_A\rho}$, where $M_{n,pol}$ corresponds to the number-average molecular weight of the block determined by ^{1}H NMR spectroscopy.

The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_c(q,R_s) = \Phi(qR_s)exp\left(-\frac{q^2\sigma^2}{2}\right) \quad \text{S12}$$

Where $\Phi(qR_s) = \frac{3\left[sin(qR_s) - qR_scos(qR_s)\right]}{(qR_s)^3}$. A sigmoidal interface between the two blocks was assumed for the spherical micelle form factor (equation S12). This is described by the exponent term with a width σ accounting for a decaying scattering length density at the micellar interface. This σ value was fixed at 2.2 during fitting.

The form factor amplitude of the spherical micelle corona is:

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s}\mu_c(r)\frac{sin(qr)}{qr}r^2dr}{\int_{R_s}^{R_s+2s}\mu_c(r)r^2dr}exp\left(-\frac{q^2\sigma^2}{2}\right) \quad \text{S13}$$

The radial profile, $\mu_c(r)$, can be expressed by a linear combination of two cubic b splines, with two fitting parameters *s* and *a* corresponding to the width of the profile and the weight coefficient, respectively. This information can be found elsewhere,[3,4] as can the approximate integrated form of Equation S13. The self-correlation term for the corona block is given by the Debye function:

$$F_c(q,R_g) = \frac{2\left[\exp\left(-q^2R_g^2\right) - 1 + q^2R_g^2\right]}{q^4R_g^2} \qquad \text{S14}$$

Where R_g is the radius of gyration of the PNMEP coronal block. The aggregation number of the spherical micelle is:

$$N_s = (1 - x_{sol})\frac{\frac{4}{3}\pi R_s^3}{V_s} \qquad \text{S15}$$

Where x_{sol} is the volume fraction of solvent in the PLMA micelle core. An effective structure factor expression proposed for interacting spherical micelles[5] has been used in equation S1:

$$S_s(q) = 1 + \frac{A_{s\_mic}^{\ av}(q)^2\left[S_{PY}(q,R_{PY},f_{PY}) - 1\right]}{F_{s\_mic}(q)} \qquad \text{S16}$$

Herein the form factor of the average radial scattering length density distribution of micelles is used as $A_{s\_mic}^{\ av}(q) = N_s\left[\beta_s A_s(q,R_s) + \beta_c A_c(q)\right]$ and $S_{PY}(q,R_{PY},f_{PY})$ is a hard-sphere interaction structure factor based on the Percus-Yevick approximation,[6] where R_{PY} is the interaction radius and f_{PY} is the hard-sphere volume fraction. A polydispersity for one parameter (R_s) is assumed for the micelle model which is described by a Gaussian distribution. Thus, the polydispersity function in Equation S1 can be replaced as:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{R_s}^2}} exp\left(-\frac{(r_1 - R_s)^2}{2\sigma_{R_s}^2}\right) \qquad \text{S17}$$

Where σ_{R_s} is the standard deviation for R_s. In accordance with equation S2, the number density per unit volume for the micelle model is expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \qquad \text{S18}$$

Where φ is the total volume fraction of copolymer in the spherical micelles and $V(r_1)$ is the total *volume* of copolymer in a spherical micelle $\left[V(r_1) = (V_s + V_c)N_s(r_1)\right]$.

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