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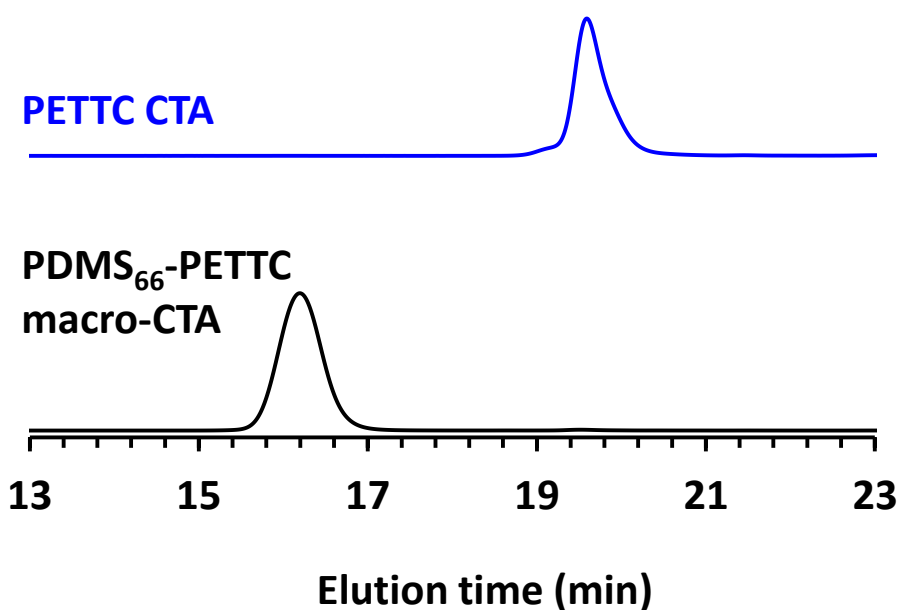
## Supporting information for:

### 'RAFT Dispersion Polymerization in Silicone Oil'

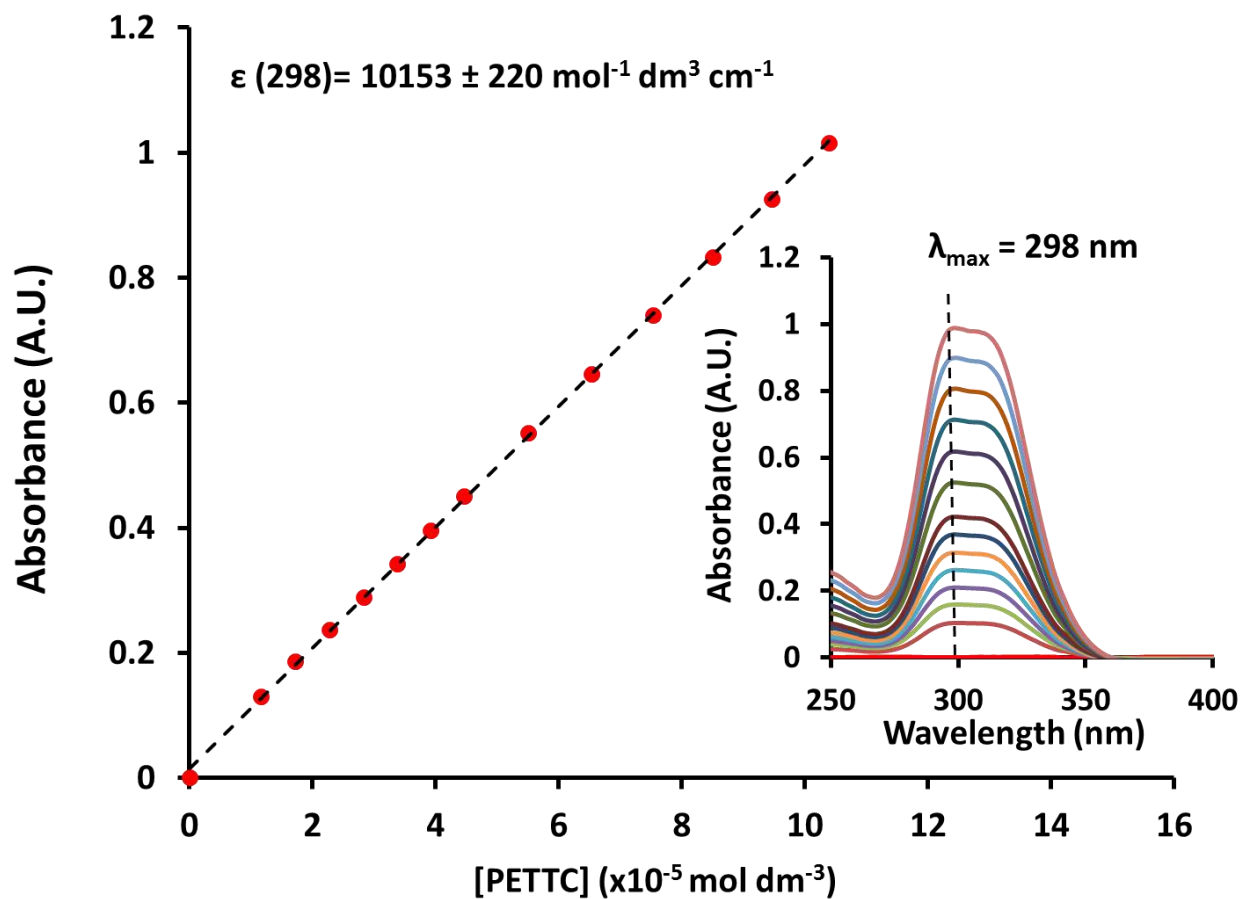
Matthew J. Rymaruk,<sup>a</sup> Saul J. Hunter,<sup>a</sup> Cate T. O'Brien,<sup>a</sup> Steven L. Brown,<sup>b</sup> Clive N. Williams,<sup>b</sup>  
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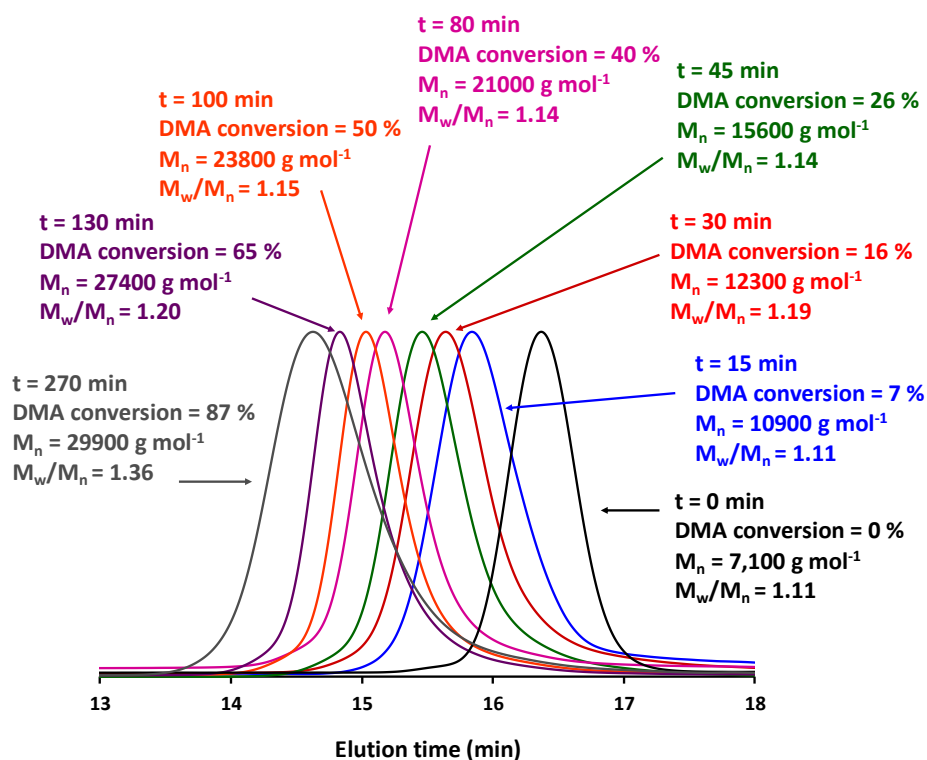
*b.* Scott Bader Company Ltd, Wollaston, Wellingborough, Northamptonshire, NN29 7RL, UK.



**Figure S1.** Uncalibrated THF GPC chromatograms obtained using a UV detector operating at 298 nm for (i) PETTC CTA (blue trace) and (ii) PDMS<sub>66</sub>-TTC macro-CTA after purification by silica column chromatography followed by a methanol wash (black trace). The absence of any PETTC signal in the PDMS<sub>66</sub>-TTC macro-CTA chromatogram indicates complete removal of this starting material.



**Figure S2.** Beer-Lambert calibration curve constructed for PETTC RAFT agent at a  $\lambda_{\text{max}}$  of 298 nm in dichloromethane.



**Figure S3.** THF GPC chromatograms recorded at various intermediate monomer conversions from the polymerization of DMA in D5 silicone oil using a PDMS<sub>66</sub> macro-CTA at 90 °C, targeting a final diblock copolymer composition of PDMS<sub>66</sub>-PDMA<sub>200</sub> at 25 % w/w solids. DMA conversions were determined at each time point by <sup>1</sup>H NMR analysis in CDCl<sub>3</sub>

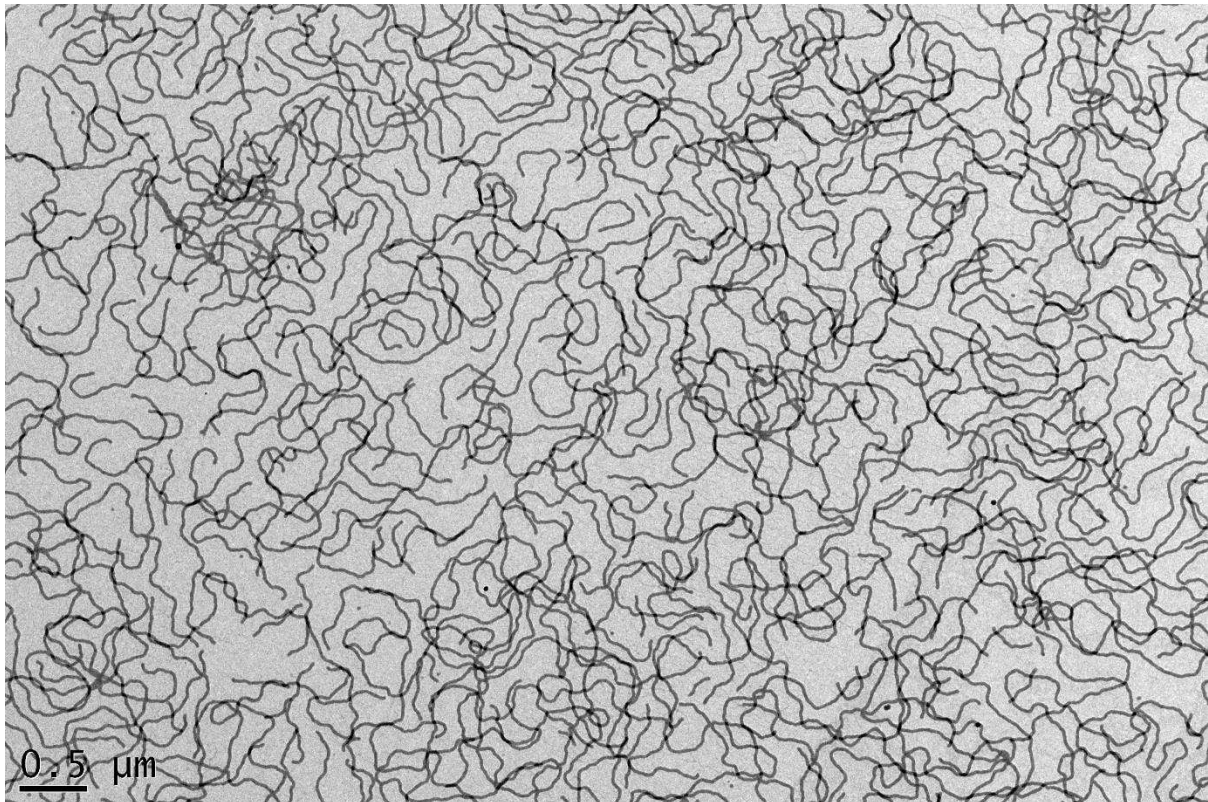
**Table S1.** Summary of the target diblock copolymer compositions, copolymer concentrations, DMA conversions, molecular weight data and final copolymer morphology assignments obtained for the series of PDMS<sub>66</sub>-PDMA<sub>x</sub> diblock copolymers used to construct the phase diagram shown in **Figure 4**.

Target Diblock Composition	Solids % w/w	Conv. <sup>a</sup> %	Actual PDMA DP	$M_n$ g mol <sup>-1</sup>	$M_w/M_n$	Morphology by TEM
PDMS <sub>66</sub> -PDMA <sub>30</sub>	30	98	29	14,400	1.14	Spheres
PDMS <sub>66</sub> -PDMA <sub>60</sub>	30	97	58	18,700	1.13	Mixed
PDMS <sub>66</sub> -PDMA <sub>65</sub>	30	97	63	19,700	1.11	Mixed
PDMS <sub>66</sub> -PDMA <sub>65</sub>	30	97	63	20,300	1.14	Mixed
PDMS <sub>66</sub> -PDMA <sub>95</sub>	30	96	91	23,200	1.18	Mixed
PDMS <sub>66</sub> -PDMA <sub>110</sub>	30	95	105	25,700	1.17	Worms
PDMS <sub>66</sub> -PDMA <sub>118</sub>	30	95	112	26,700	1.17	Worms
PDMS <sub>66</sub> -PDMA <sub>130</sub>	30	94	122	26,100	1.22	Mixed
PDMS <sub>66</sub> -PDMA <sub>170</sub>	30	95	162	33,400	1.19	Mixed
PDMS <sub>66</sub> -PDMA <sub>180</sub>	30	95	171	35,600	1.19	Vesicles
PDMS <sub>66</sub> -PDMA <sub>20</sub>	25	95	19	12,600	1.17	No PISA
PDMS <sub>66</sub> -PDMA <sub>30</sub>	25	95	29	14,300	1.13	Spheres
PDMS <sub>66</sub> -PDMA <sub>50</sub>	25	97	49	16,900	1.14	Spheres
PDMS <sub>66</sub> -PDMA <sub>70</sub>	25	94	66	18,800	1.15	Mixed

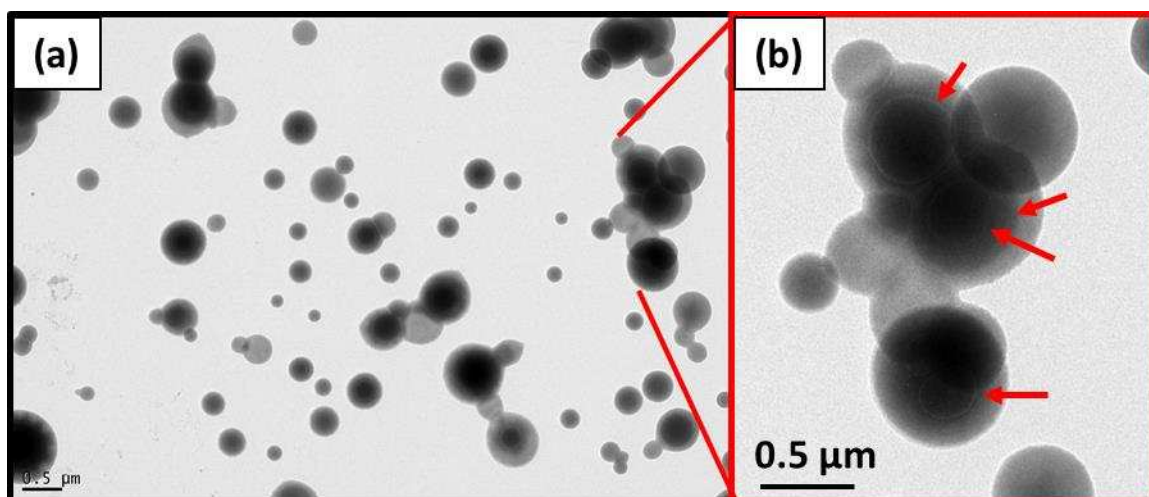
**Table S1 Continued**

PDMS <sub>66</sub> -PDMA <sub>90</sub>	25	95	86	22,700	1.13	Mixed
PDMS <sub>66</sub> -PDMA <sub>100</sub>	25	95	95	23,200	1.17	Mixed
PDMS <sub>66</sub> -PDMA <sub>105</sub>	25	95	100	24,300	1.18	Worms
PDMS <sub>66</sub> -PDMA <sub>110</sub>	25	95	105	24,300	1.17	Worms
PDMS <sub>66</sub> -PDMA <sub>120</sub>	25	95	114	25,200	1.22	Mixed
PDMS <sub>66</sub> -PDMA <sub>150</sub>	25	91	137	28,200	1.23	Mixed
PDMS <sub>66</sub> -PDMA <sub>160</sub>	25	93	149	34,100	1.24	Mixed
PDMS <sub>66</sub> -PDMA <sub>170</sub>	25	93	158	32,800	1.20	Mixed
PDMS <sub>66</sub> -PDMA <sub>180</sub>	25	94	169	37,200	1.21	Vesicles
PDMS <sub>66</sub> -PDMA <sub>190</sub>	25	90	171	37,400	1.24	Vesicles
PDMS <sub>66</sub> -PDMA <sub>200</sub>	25	93	186	38,300	1.23	Vesicles
PDMS <sub>66</sub> -PDMA <sub>220</sub>	25	92	202	41,900	1.24	Vesicles
PDMS <sub>66</sub> -PDMA <sub>20</sub>	20	88	18	12,100	1.16	NO PISA
PDMS <sub>66</sub> -PDMA <sub>30</sub>	20	90	27	15,800	1.15	Spheres
PDMS <sub>66</sub> -PDMA <sub>50</sub>	20	89	45	18,800	1.14	Spheres
PDMS <sub>66</sub> -PDMA <sub>70</sub>	20	91	64	20,300	1.20	Spheres
PDMS <sub>66</sub> -PDMA <sub>90</sub>	20	92	83	20,700	1.17	Mixed
PDMS <sub>66</sub> -PDMA <sub>100</sub>	20	89	89	23,500	1.19	Mixed
PDMS <sub>66</sub> -PDMA <sub>110</sub>	20	92	101	24,400	1.27	Mixed
PDMS <sub>66</sub> -PDMA <sub>120</sub>	20	93	112	25,700	1.27	Mixed
PDMS <sub>66</sub> -PDMA <sub>130</sub>	20	92	120	28,600	1.21	Mixed
PDMS <sub>66</sub> -PDMA <sub>150</sub>	20	91	137	27,800	1.33	Mixed
PDMS <sub>66</sub> -PDMA <sub>160</sub>	20	93	149	27,800	1.36	Mixed
PDMS <sub>66</sub> -PDMA <sub>170</sub>	20	93	158	32,500	1.26	Mixed
PDMS <sub>66</sub> -PDMA <sub>180</sub>	20	94	169	32,700	1.29	Vesicles
PDMS <sub>66</sub> -PDMA <sub>190</sub>	20	91	173	35,500	1.24	Vesicles
PDMS <sub>66</sub> -PDMA <sub>200</sub>	20	91	182	35,100	1.32	Vesicles
PDMS <sub>66</sub> -PDMA <sub>220</sub>	20	90	198	36,400	1.32	Vesicles
PDMS <sub>66</sub> -PDMA <sub>40</sub>	15	92	37	15,200	1.10	Spheres
PDMS <sub>66</sub> -PDMA <sub>80</sub>	15	89	71	20,500	1.14	Spheres
PDMS <sub>66</sub> -PDMA <sub>110</sub>	15	85	94	24,200	1.11	Spheres
PDMS <sub>66</sub> -PDMA <sub>120</sub>	15	88	106	24,900	1.16	Mixed
PDMS <sub>66</sub> -PDMA <sub>130</sub>	15	91	118	27,100	1.16	Spheres
PDMS <sub>66</sub> -PDMA <sub>150</sub>	15	89	134	23,100	1.36	Mixed
PDMS <sub>66</sub> -PDMA <sub>170</sub>	15	89	151	29,900	1.20	Mixed
PDMS <sub>66</sub> -PDMA <sub>180</sub>	15	90	162	28,000	1.31	Mixed
PDMS <sub>66</sub> -PDMA <sub>190</sub>	15	90	171	27,100	1.34	Vesicles
PDMS <sub>66</sub> -PDMA <sub>200</sub>	15	80	160	28,200	1.38	Mixed
PDMS <sub>66</sub> -PDMA <sub>220</sub>	15	86	189	34,200	1.29	Vesicles
PDMS <sub>66</sub> -PDMA <sub>50</sub>	10	83	42	16,900	1.14	Spheres
PDMS <sub>66</sub> -PDMA <sub>80</sub>	10	80	64	20,100	1.16	Spheres
PDMS <sub>66</sub> -PDMA <sub>100</sub>	10	79	79	19,900	1.22	Spheres
PDMS <sub>66</sub> -PDMA <sub>120</sub>	10	80	96	24,100	1.19	Spheres
PDMS <sub>66</sub> -PDMA <sub>150</sub>	10	79	119	27,000	1.20	Mixed
PDMS <sub>66</sub> -PDMA <sub>200</sub>	10	83	166	31,900	1.23	Mixed
PDMS <sub>66</sub> -PDMA <sub>220</sub>	10	87	191	27,100	1.41	Vesicles

<sup>a</sup> <sup>1</sup>H NMR spectroscopy studies conducted in CDCl<sub>3</sub>



**Figure S4.** Lower magnification TEM image of PDMS<sub>66</sub>-PDMA<sub>100</sub> worms synthesized at 25 % w/w in silicone oil (D5) and imaged at 0.05 % w/w. Image analysis using ImageJ software indicated that the lower limit for the mean worm contour length was approximately 1500 nm. The scale bar corresponds to 0.5 μm.



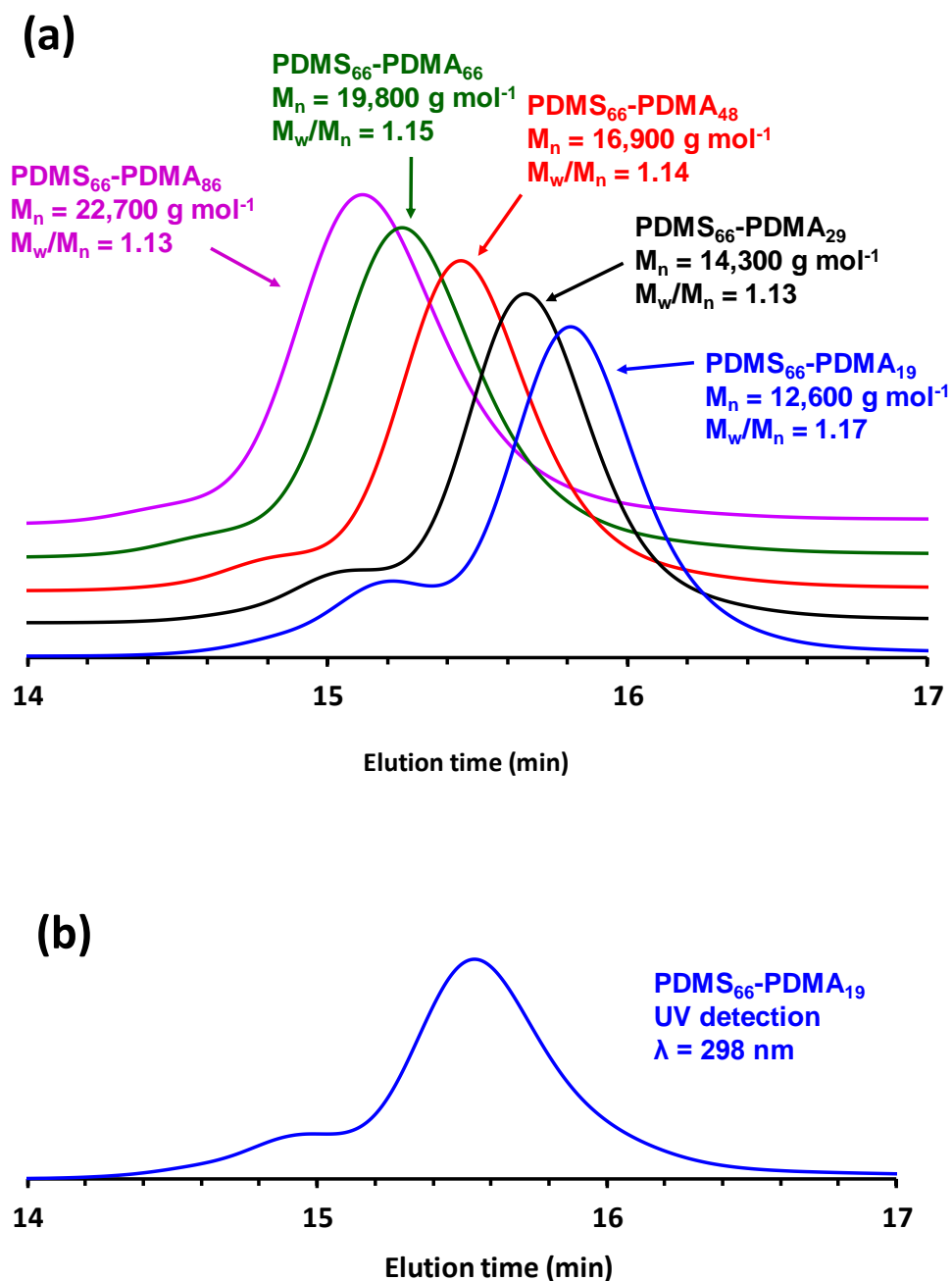
**Figure S5.** (a) Representative TEM image of PDMS<sub>66</sub>-PDMA<sub>186</sub> vesicles synthesised at 25 % w/w solids in D5 and imaged at ~ 0.20 % w/w. (b) higher magnification image for the 'red box' area indicated in (a) suggesting the presence of multilamellar vesicles

**Table 2. Structural parameters obtained from SAXS data fits for the patterns shown in Figure 5 (see main manuscript): sphere or worm core radius ( $R_c$ ), standard deviation of the core radius ( $\sigma_{core}$ ), radius of gyration of the PDMS<sub>66</sub> corona chains ( $R_g$ ), solvent volume fraction in the core ( $X_{sol}$ ), vesicle membrane thickness ( $T_m$ ), standard deviation of the vesicle membrane thickness ( $\sigma_{Tm}$ ), overall vesicle radius ( $R_o$ ) and aggregation number ( $N_{agg}$ )**

<b>Copolymer composition</b>	<b>Morphology</b>	<b><math>R_c</math> / nm</b>	<b><math>\sigma_{core}/nm</math></b>	<b><math>R_g/nm</math></b>	<b><math>X_{sol}</math></b>	<b><math>T_m/nm</math></b>	<b><math>\sigma_{Tm}/nm</math></b>	<b><math>R_o/nm</math></b>	<b><math>N_{agg}</math></b>
PDMS <sub>66</sub> -PDMA <sub>49</sub>	Spheres	8.3	0.9	1.7	0	-	-	-	196
PDMS <sub>66</sub> -PDMA <sub>100</sub>	Worms	9.4	1.1	1.6	0	-	-	-	*
PDMS <sub>66</sub> -PDMA <sub>191</sub>	Vesicles	-	-	1.6	0	20.7	2.6	102.4	48,337

\* The mean aggregation number for the worms could not be determined because the mean worm contour length was too large ( $\gg 1 \mu m$ , see Figure S4) to be determined by SAXS.





**Figure S6.** (a) GPC traces obtained using a refractive index (RI) detector (THF eluent; calibrated using a series of near-monodisperse PMMA standards) recorded for a series of PDMS<sub>66</sub>-PDMA<sub>x</sub> diblock copolymers prepared at 25 % w/w solids in D5 silicone oil. (b) Gel permeation chromatogram obtained using a UV detector ( $\lambda = 298 \text{ nm}$ ) for the PDMS<sub>66</sub>-PDMA<sub>19</sub> diblock copolymer [shown as the blue trace in (a)]. This shows that the high molecular weight shoulder at around 15 min corresponds to chains that contain trithiocarbonate-based RAFT end-groups. [N.B. The RI and UV detectors were connected in series, so the peak elution time observed for the UV chromatogram is delayed by  $\sim 30 \text{ s}$  relative to that for the RI chromatogram].

## SAXS models

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:

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

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:

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

where  $V(r_1, \dots, r_k)$  is volume of the nano-object and  $\varphi$  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  $s(q) = 1$ .

### ***Spherical micelle model***

The spherical micelle form factor for Equation S1 is given by: <sup>1</sup>

$$F_{s\_mic}(q) = N_s^2 \beta_s^2 A_s^2(q, R_s) + N_s \beta_c^2 F_c(q, R_g) + N_s(N_s - 1) \beta_c^2 A_c^2(q) \\ + 2N_s^2 \beta_s \beta_c A_s(q, R_s) A_c(q) \quad S3$$

where  $R_s$  is the core radius of the spherical micelle,  $R_g$  is the radius of gyration of the PDMS 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  $\beta_c = V_c(\xi_c - \xi_{sol})$ , respectively. Here  $\xi_s$ ,  $\xi_c$  and  $\xi_{sol}$  are the X-ray scattering length densities of the core block ( $\xi_{PDMA} = 10.12 \times 10^{10} \text{ cm}^{-2}$ ), the corona block ( $\xi_{PDMS} = 8.89 \times 10^{10} \text{ cm}^{-2}$ ) and the solvent ( $\xi_{sol} = 8.78 \times 10^{10} \text{ cm}^{-2}$ ), respectively.  $V_s$  and  $V_c$  are volumes of the core block ( $V_{PDMA}$ ) and the corona block ( $V_{PDMS}$ ), respectively. The volumes were obtained 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  $^1\text{H}$  NMR spectroscopy. The density of PDMA was taken from the literature<sup>2</sup> ( $\rho_{PDMA} = 1.09 \text{ g cm}^{-3}$ ) while that for PDMS ( $\rho_{PDMS} = 0.97 \text{ g cm}^{-3}$ ) was determined using an Anton Paar density meter DMA 5000M, The sphere form factor amplitude is used for the amplitude of the core self-term:

$$A_s(q, R_s) = \Phi(qR_s) \exp\left(-\frac{q^2 \sigma^2}{2}\right) \quad \text{S4}$$

where  $\Phi(qR_s) = \frac{3[\sin(qR_s) - qR_s \cos(qR_s)]}{(qR_s)^3}$ .

A sigmoidal interface between the two blocks was assumed for the spherical micelle form factor [Equation S3]. This is described by the exponent term with a width  $\sigma$  accounting for a decaying scattering length density at the micellar interface. This  $\sigma$  value was fixed at 2.5 during fitting.

The form factor amplitude of the spherical micelle corona is:

$$A_c(q) = \frac{\int_{R_s}^{R_s+2s} \mu_c(r) \frac{\sin(qr)}{qr} r^2 dr}{\int_{R_s}^{R_s+2s} \mu_c(r) r^2 dr} \exp\left(-\frac{q^2 \sigma^2}{2}\right) \quad \text{S5}$$

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,<sup>3,4</sup> as can the approximate integrated form of Equation S5. The self-correlation term for the corona block is given by the Debye function:

$$F_c(q, R_g) = \frac{2 \left[ e^{(-q^2 R_g^2)} - 1 + q^2 R_g^2 \right]}{q^4 R_g^4} \quad S6$$

where  $R_g$  is the radius of gyration of the PDMS coronal block. The aggregation number of the spherical micelle is:

$$N_s = (1 - x_{sol}) \frac{\frac{4}{3} \pi R_s^3}{V_s} \quad S7$$

where  $x_{sol}$  is the volume fraction of solvent in the PDMA micelle core.

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 represented as:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{R_s}^2}} \exp\left(-\frac{(r_1 - R_s)^2}{2\sigma_{R_s}^2}\right) \quad S8$$

where  $\sigma_{R_s}$  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:

$$N = \frac{\varphi}{\int_0^\infty V(r_1) \Psi(r_1) dr_1} \quad S9$$

where  $\varphi$  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 [ $V(r_1) = (V_s + V_c)N_s(r_1)$ ].

The model fitting to the final SAXS pattern for the PDMS<sub>66</sub>-PDMA<sub>49</sub> spheres indicated  $\varphi = 0.0$ ,  $R_{PY} = 8.25$  nm and  $f_{PY} = 0.009$ , which is consistent with the expected volume fraction of polymer (0.0093). The experimental  $R_g$  obtained from this fitting for the coronal PDMS chains (1.7 nm) is also physically reasonable, since it is close to the theoretically calculated parameter. Assuming that the contour length of a PDMS monomer is 0.243 nm (two silicon-oxygen bonds in all-trans conformation), the total contour length of a PDMS<sub>66</sub> block,  $L_{PDMS66} = 66 \times 0.243$  nm = 16.04 nm. Given a mean Kuhn length of 1.13 nm [based on the known literature value for PDMS<sup>5</sup>], an estimated unperturbed radius of gyration,  $R_g = (16.04 \times 1.13/6)^{0.5}$ , or 1.74 nm is determined.

### ***Worm model***

The worm-like micelle form factor in Equation (S1) is expressed as:<sup>1</sup>

$$F_{w\_mic}(q) = N_w^2 \beta_s^2 F_{sw}(q) + N_w \beta_c^2 F_c(q, R_g) + N_w(N_w - 1) \beta_c^2 S_{cc}(q) + 2N_w^2 \beta_s \beta_c S_{sc}(q) \quad S10$$

where the core block and the corona block X-ray scattering length contrast is given by  $\beta_s = V_s(\xi_s - \xi_{sol})$  and  $\beta_c = V_c(\xi_c - \xi_{sol})$ , respectively. Here,  $\xi_s$ ,  $\xi_c$  and  $\xi_{sol}$  are the X-ray scattering length densities of the core block ( $\xi_{PDMA} = 10.12 \times 10^{10}$  cm<sup>-2</sup>), the corona block ( $\xi_{PDMS} = 8.89 \times 10^{10}$  cm<sup>-2</sup>) and the D5 solvent ( $\xi_{sol} = 8.78 \times 10^{10}$  cm<sup>-2</sup>), respectively.  $V_s$  and  $V_c$  are the volumes of the core block ( $V_{PDMA}$ ) and the corona block ( $V_{PDMS}$ ), respectively. The volumes were obtained from  $V = \frac{M_{n,poly}}{N_A \rho}$  using the solid-state densities of PDMA ( $\rho_{PDMA} = 1.09$  g cm<sup>-3</sup>) and PDMS ( $\rho_{PDMS} = 0.97$  g cm<sup>-3</sup>), where  $M_{n,pol}$  corresponds to the number-average molecular weight of each block determined by <sup>1</sup>H NMR spectroscopy. The self-correlation term for the worm-like micelle core of radius  $R_{sw}$  is:

$$F_{sw}(q) = F_{worm}(q, L_w, b_w) A_{cs_{worm}}^2(q, R_{sw}) \quad S11$$

which is a product of a core cross-section term:

$$F_{cs_{worm}}(q, R_g) = A_{cs_{worm}}^2(q, R_s) = \left[ 2 \frac{J_1(qR_{sw})}{qR_{sw}} \right]^2 \quad S12$$

where  $J_1$  is the first-order Bessel function of the first kind, and a form factor  $F_{worm}(q, L_w, b_w)$  for self-avoiding semi-flexible chains represent the worm-like micelle, where  $b_w$  is the worm Kuhn length and  $L_w$  is the mean worm contour length. A complete expression for the chain form factor can be found elsewhere.<sup>6</sup> The self-correlation term for the corona block is given by the Debye function shown in Equation S6. The interference cross-term between the worm micelle core and the corona chain is given by:

$$S_{sc}(q) = \Psi^2(qR_g) J_0^2[q(R_{sw} + R_g)] F_{worm}(q, L_w, b_w) \quad S13$$

where  $\Psi(qR_g) = \frac{1 - \exp(-q^2 R_g^2)}{(qR_g)^2}$  is the form factor amplitude of the corona chain,  $R_g$  is the radius of gyration of PDMA corona block and  $J_0$  is the zero-order Bessel function of the first kind. The interference term between the worm corona chains is:

$$S_{cc}(q) = \Psi(qR_g) A_{cs_{worm}} J_0[q(R_{sw} + R_g)] F_{worm}(q, L_w, b_w) \quad S14$$

The mean aggregation number for worm-like micelles is given by:

$$N_w = (1 - x_{sol}) \frac{\pi R_{sw}^2 L_w}{V_s} \quad S15$$

where  $x_{sol}$  is the volume fraction of solvent within the worm-like micelle core. Possible semi-spherical caps at the ends of each worm are not considered in this form factor. It is also assumed that  $S(q) = 1$  at sufficiently low copolymer concentrations (e.g. 1.0 % w/w).

### **Vesicle model**

The vesicle form factor in Equation (S1) is expressed as:<sup>7</sup>

$$F_{ves}(q) = N_v^2 \beta_m^2 A_m^2(q) + N_v \beta_{vc}^2 F_c(q, R_g) + N_v(N_v - 1) \beta_{vc}^2 A_{vc}^2(q) + 2N_v^2 \beta_m \beta_{vc} A_m(q) A_{vc}(q) \quad S16$$

The X-ray scattering length contrast for the membrane-forming block (PDMA) and the coronal stabilizer block (PDMS) is given by  $\beta_m = V_m(\xi_m - \xi_{sol})$  and  $\beta_{vc} = V_{vc}(\xi_{vc} - \xi_{sol})$ , respectively, where  $\xi_m$ ,  $\xi_{vc}$  and  $\xi_{sol}$  are the X-ray scattering length densities of the membrane-forming block ( $\xi_{PDMA} = 10.12 \times 10^{10} \text{ cm}^{-2}$ ), the coronal stabilizer block ( $\xi_{PDMS} = 8.89 \times 10^{10} \text{ cm}^{-2}$ ) and the solvent ( $\xi_{sol} = 8.78 \times 10^{10} \text{ cm}^{-2}$ ).  $V_m$  and  $V_{vc}$  are the volumes of the membrane-forming block and the coronal stabilizer block, respectively. Using the molecular weights of the PDMA and PDMS blocks and their respective mass densities ( $\rho_{PDMA} = 1.09 \text{ g cm}^{-3}$  and  $\rho_{PDMS} = 0.97 \text{ g cm}^{-3}$ ), 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 <sup>1</sup>H NMR spectroscopy. The amplitude of the membrane self-term is:

$$A_m(q) = \frac{V_{out}\varphi(qR_{out}) - V_{in}\varphi(qR_{in})}{V_{out} - V_{in}} e^{\left(-\frac{q^2\sigma_{in}^2}{2}\right)} \quad S17$$

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 S17 differs from that reported in the original work.<sup>7</sup> More specifically, the exponent term in Equation S17 represents a sigmoidal interface between the blocks, with a width  $\sigma_{in}$  accounting for a decaying scattering length density at the membrane surface. The numerical value of  $\sigma_{in}$  was fixed at 2.5. The mean vesicle aggregation number,  $N_v$ , is given by:

$$N_v = (1 - x_{sol}) \frac{V_{out} - V_{in}}{V_m} \quad S18$$

where  $x_{sol}$  is the solvent (i.e. D5) 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:

$$A_{vc}(q) = \Psi(qR_g) \frac{1}{2} \left[ \frac{\sin[q(R_{out} + R_g)]}{q(R_{out} + R_g)} + \frac{\sin[q(R_{in} - R_g)]}{q(R_{in} - R_g)} \right] \quad S19$$

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



$$\Psi(qR_g) = \frac{1 - \exp(-qR_g)}{(qR_g)^2} \quad \text{S20}$$

Again, the experimental  $R_g$  value of 1.6 nm for the PDMS<sub>66</sub> coronal block is comparable to the estimated value. The latter can be calculated from the total contour length of the PDMS<sub>66</sub> block,  $L_{\text{PDMS66}} = 66 \times 0.243 \text{ nm} = 16.04 \text{ nm}$  (since the projected contour length per PDMS monomer repeat unit is defined by two silicon-oxygen bonds in an all-trans conformation, or 0.243 nm) and the Kuhn length of 1.13 nm based on the known literature value for PDMS<sup>5</sup> result in an approximate  $R_g$  of  $(16.83 \times 1.13/6)^{0.5} = 1.74 \text{ nm}$ .

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:

$$\Psi(r_1, r_2) = \frac{1}{\sqrt{2\pi\sigma_{R_m}^2}} \exp\left(-\frac{(r_1 - R_m)^2}{2\sigma_{R_m}^2}\right) \frac{1}{\sqrt{2\pi\sigma_{T_m}^2}} \exp\left(-\frac{(r_1 - T_m)^2}{2\sigma_{T_m}^2}\right) \quad \text{S21}$$

where  $\sigma_{R_m}$  and  $\sigma_{T_m}$  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:

$$N = \frac{\varphi}{\int_0^\infty \int_0^\infty V(r_1, r_2) \Psi(r_1, r_2) dr_1 dr_2} \quad \text{S22}$$

where  $\varphi$  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.<sup>8</sup>

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