

Effect of Block Ratio and Structure on the Thermosensitivity of Double and Triple Betaine Block Copolymers

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Table S1. Experimental conditions for the synthesis of PGLBT-*b*-PSPEs via RAFT polymerization in water at 70 °C (sum of DP_{target}: 300)

Sample	GLBT ₁₄₉ - <i>b</i> -SPE ₁₆₁		GLBT ₁₀₀ - <i>b</i> -SPE ₂₄₅		GLBT ₇₄ - <i>b</i> -SPE ₂₇₇		GLBT ₄₉ - <i>b</i> -SPE ₂₂₉	
Steps	1	2	1	2	1	2	1	2
Monomer	GLBT	SPE	GLBT	SPE	GLBT	SPE	GLBT	SPE
DP _{target}	150	150	100	200	75	225	50	250
m _{monomer} (g)	1.427	1.851	0.951	2.469	0.713	2.814	0.476	3.086
m _{CTA} (g)	0.015		0.015		0.015		0.015	
m _{VA-044} (g)	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³	0.7 × 10 ⁻³
Reaction time (h)	3	3	3	3	3	3	3	3
V _{solvent} (mL) ^[a]	2.2	2.7	1.7	4.2	1.3	4	0.75	4.25
[M] ₀ (mol/L)	3.01	2.45	2.60	2.10	2.55	2.52	2.95	2.60
[CTA] ₀ /[I] ₀	20	20	20	20	20	20	20	20
Cumulative L (%)	95.3	90.8	95.3	90.8	95.3	90.8	95.3	90.8

[a] is the sum of the volume of the solvent added in the first and the next step

Table S2. Experimental conditions for the synthesis of PGLBT-*b*-PSPEs via RAFT polymerization in water at 70 °C (sum of DP_{target}: 600)

Sample	GLBT ₂₉₇ - <i>b</i> -SPE ₃₃₀		GLBT ₁₉₈ - <i>b</i> -SPE ₈₁₁		GLBT ₁₄₉ - <i>b</i> -SPE ₇₄₂		GLBT ₉₉ - <i>b</i> -SPE ₆₃₀	
Steps	1	2	1	2	1	2	1	2
Monomer	GLBT	SPE	GLBT	SPE	GLBT	SPE	GLBT	SPE
DP _{target}	300	300	200	400	150	450	100	500
m _{monomer} (g)	1.902	2.493	1.268	3.292	0.951	3.703	0.634	3.086
m _{CTA} (g)	0.01		0.01		0.01		0.01	
m _{VA-044} (g)	0.5 x 10 ⁻³	0.7 x 10 ⁻³	0.5 x 10 ⁻³	1.0 x 10 ⁻³	0.5 x 10 ⁻³	1.0 x 10 ⁻³	0.5 x 10 ⁻³	1.0 x 10 ⁻³
Reaction time (h)	6	6	6	6	6	6	6	6
V _{solvent} (mL) ^[a]	2.80	3.50	1.70	4.60	1.20	4.50	1.00	7.00
[M] ₀ (mol/L)	3.16	2.55	3.46	2.56	3.68	2.95	2.95	2.12
[CTA] ₀ /[I] ₀	20	14	20	10	20	10	20	10
Cumulative L (%)	95.3	90.8	95.3	86.6	95.3	86.6	95.3	86.7

Table S3. Experimental conditions for preparation of BAB-type PSPE-PGLBT-PSPEs via RAFT polymerization in water at 70 °C (sum of DP_{target}: 600)

Sample	SPE ₁₉₈ -GLBT ₁₉₈ -SPE ₂₁₂			SPE ₂₄₈ -GLBT ₉₉ -SPE ₂₇₇		
Steps	1	2	3	1	2	3
Monomer	SPE	GLBT	SPE	SPE	GLBT	SPE
DP _{target}	200	200	200	250	100	250
m _{monomer} (g)	2.304	1.793	2.337	3.086	0.959	3.118
m _{CTA} (g)	0.014			0.015		
m _{VA-044} (g)	0.7 x 10 ⁻³	0.7 x 10 ⁻³	0.9 x 10 ⁻³	0.7 x 10 ⁻³	1.2 x 10 ⁻³	0.7 x 10 ⁻³
Reaction time (h)	3	3	3	3	3	3
V _{solvent} (mL) ^[a]	2.70	3.20	4.20	3.60	4.10	5.60
[M] ₀ (mol/L)	3.05	2.60	2.00	3.07	1.09	1.99
[CTA] ₀ /[I] ₀	20	20	14	20	12.5	20
Cumulative L (%)	95.3	90.8	84.9	95.3	88.3	84.1

Details of DLS and SLS analysis

The normalized intensity autocorrelation function $g^{(2)}(q,t)$ is measured by

$$g^{(2)}(q, t) = \frac{\langle I^*(q, 0)I(q, t) \rangle}{\langle I(q, 0)^2 \rangle} \quad (\text{S1})$$

Then, $g^{(2)}(q,t)$ is related to the normalized electric field autocorrelation function $g^{(1)}(q,t)$ by the Siegert relation (S1),

$$g^{(2)}(q, t) = 1 + \beta |g^{(1)}(q, t)|^2 \quad (\text{S2})$$

where β is a coherence factor depending on the experimental conditions, and $g^{(1)}(q,t)$ is to be evaluated. For a polydisperse particle system, the $g^{(1)}(q,t)$ s can be written as:

$$g^{(1)}(q, t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) d\Gamma \quad (\text{S3})$$

where $G(\Gamma)$ is the intensity-based normalized distribution of decay rates $\int G(\Gamma) d\Gamma = 1$ and able to be calculated through inverse Laplace transform. (CONTIN regularization was applied by a software, BIC Particle Explorer, Brookhaven Instruments) The translational diffusion coefficient $D_t = \bar{\Gamma}/q^2$ was obtained from the slope of the decay rate $\bar{\Gamma}$ versus q^2 . The scattering vector q is

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (\text{S4})$$

where n is the refractive index of the water, λ is the wavelength of the incident laser (632.8 nm), and θ is the scattering angle. The hydrodynamic radius R_h was obtained by the Stokes-Einstein equation:

$$R_h = \frac{k_B T}{6\pi\eta D_t} \quad (S5)$$

Where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of solvent (water), respectively.

In the static light scattering (SLS) measurements, the scattering intensity were recorded over an angular range between 40° and 150° at 10° intervals. A partial Zimm equation (S5) of the inverse scattering intensity ($1/I_{ex}$) versus the square of the scattering vector q^2 at a single concentration was used to determine the radius of gyration (R_g), as follows

$$\frac{1}{I_{ex}(q)} = C(1 + \frac{R_g^2 q^2}{3}) \quad (S6)$$

where C is the arbitrary constant, and $I_{ex}(q)$ is the intensity of scattered light. Several points that were apparently discrepant from the overall results were exempted from the linear fitting.

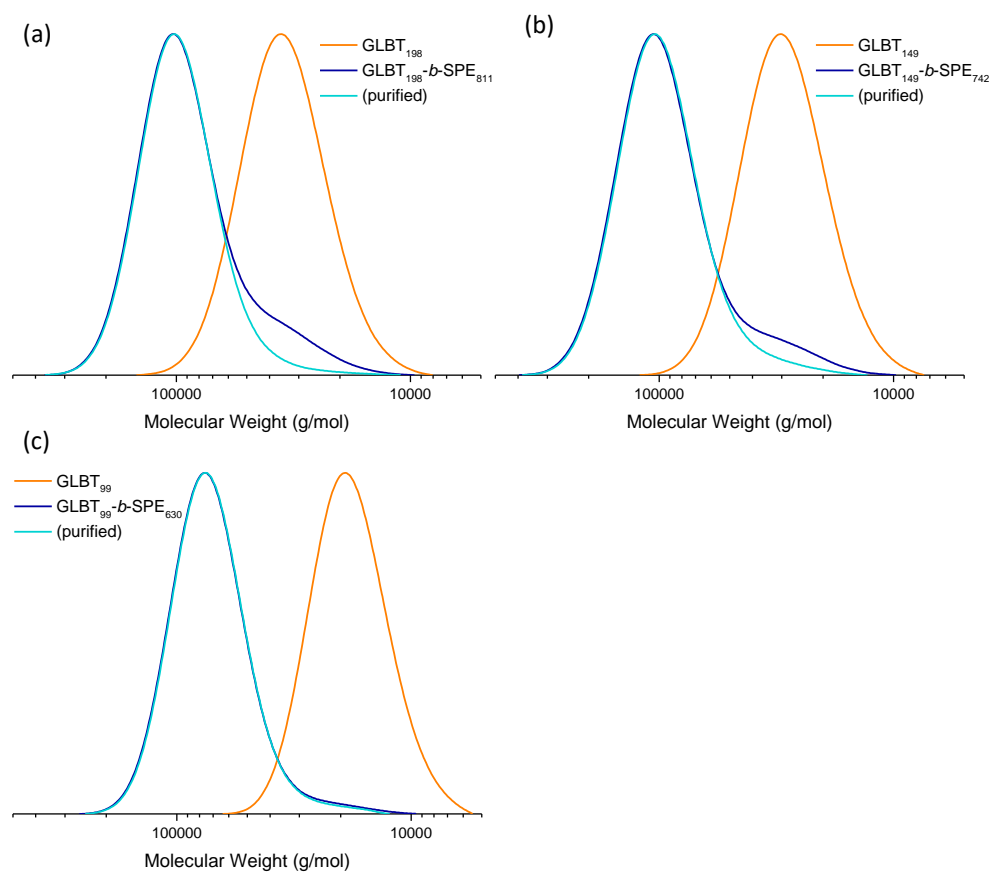


Figure S1. Molecular weight distributions of crude and purified PGLBT-*b*-PSPEs and PGLBTs as their macroCTAs (total DP_{target}: 600) (a) GLBT₁₉₈-*b*-SPE₈₁₁ (b) GLBT₁₄₉-*b*-SPE₇₄₂ (c) GLBT₉₉-*b*-SPE₆₃₀

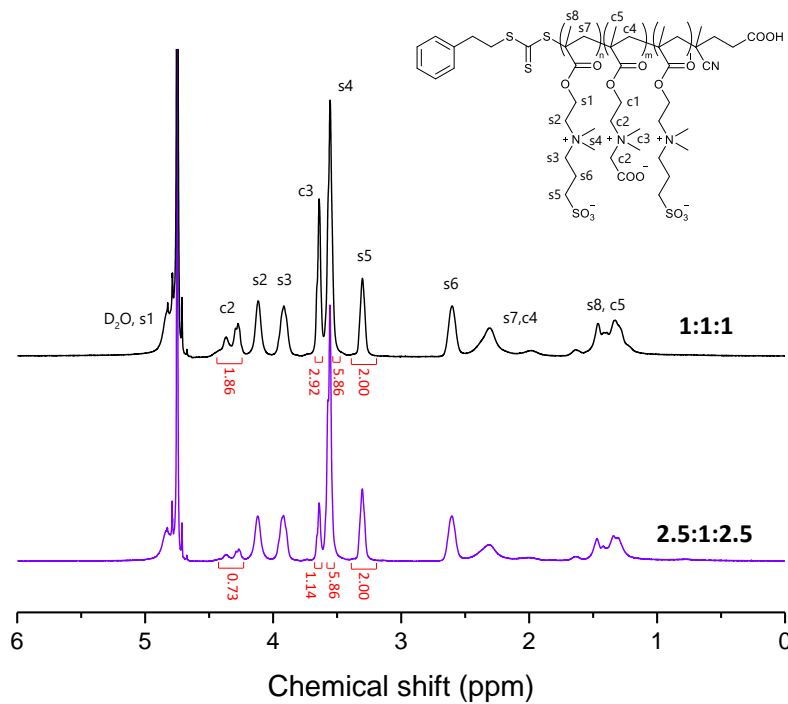


Figure S2. ^1H NMR spectra of two triblocks in D_2O at $60\text{ }^\circ\text{C}$. $\text{SPE}_{198}\text{-GLBT}_{198}\text{-SPE}_{212}$ (target ratio = 1:1:1, black line) and $\text{SPE}_{248}\text{-GLBT}_{99}\text{-SPE}_{277}$ (target ratio = 2.5:1:2.5, blue line)

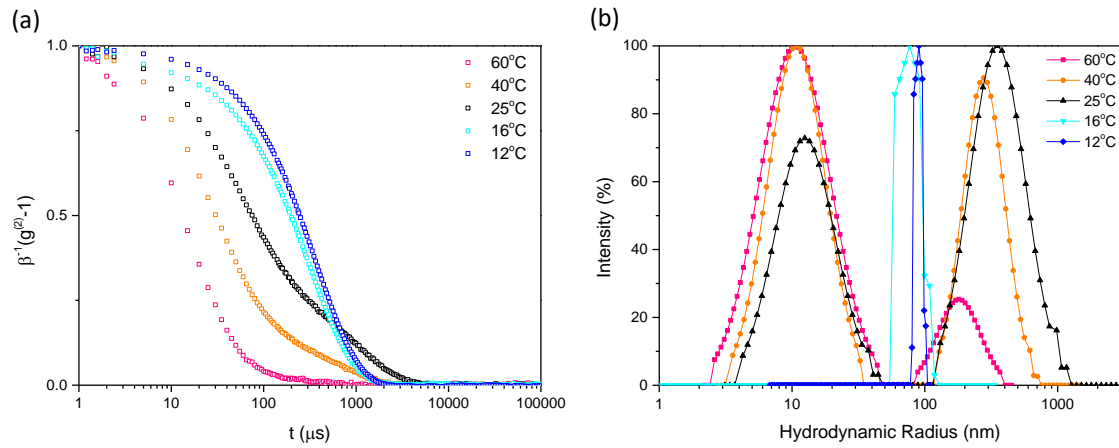


Figure S3. The autocorrelation functions of GLBT₁₄₉-*b*-SPE₇₄₂ (a) and the size distributions (b) at 5 temperatures. (conc. = 10 mg/mL)

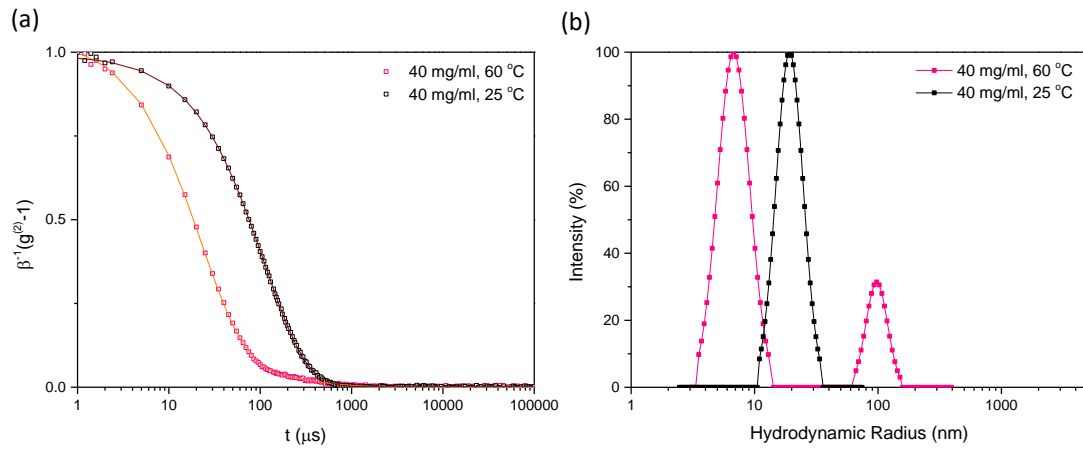


Figure S4. (a) ACFs and (b) the CONTIN analysis result of GLBT₄₉-*b*-SPE₂₂₉ solution (conc. = 40 mg/mL) measured at 25 and 60 °C, respectively.

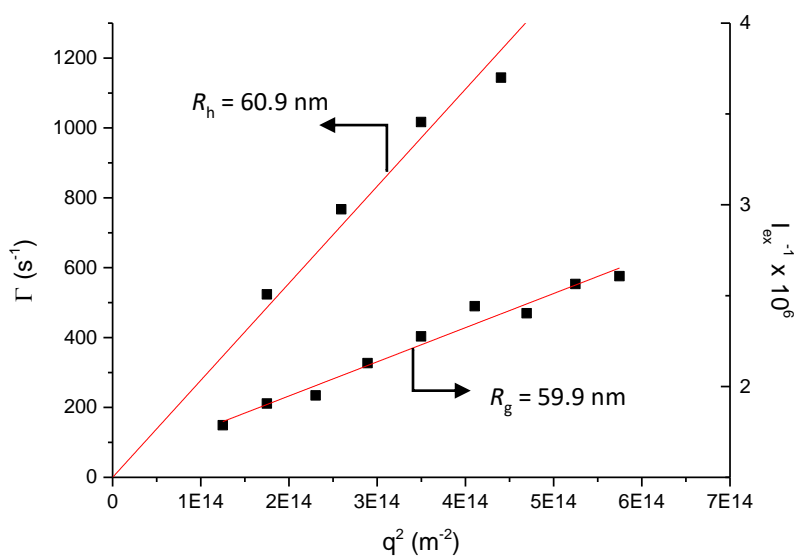


Figure S5. Angular dependent DLS and SLS measurements of (a) GLBT₉₉-b-SPE₆₃₀ at 12 °C (conc. = 10 mg/mL)

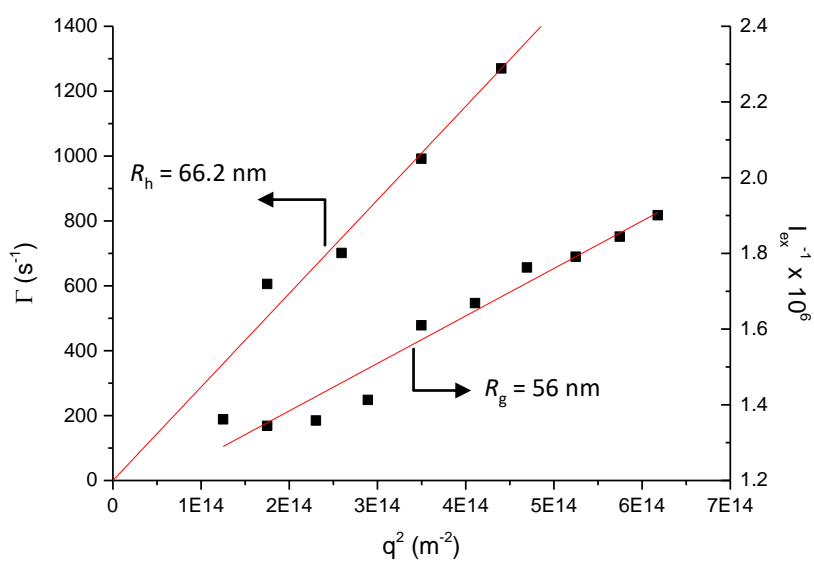


Figure S6. Angular dependent DLS and SLS measurements of (a) SPE₂₄₈-GLBT₉₉-SPE₂₇₇ at 16 °C (conc. = 2.5 mg/mL)

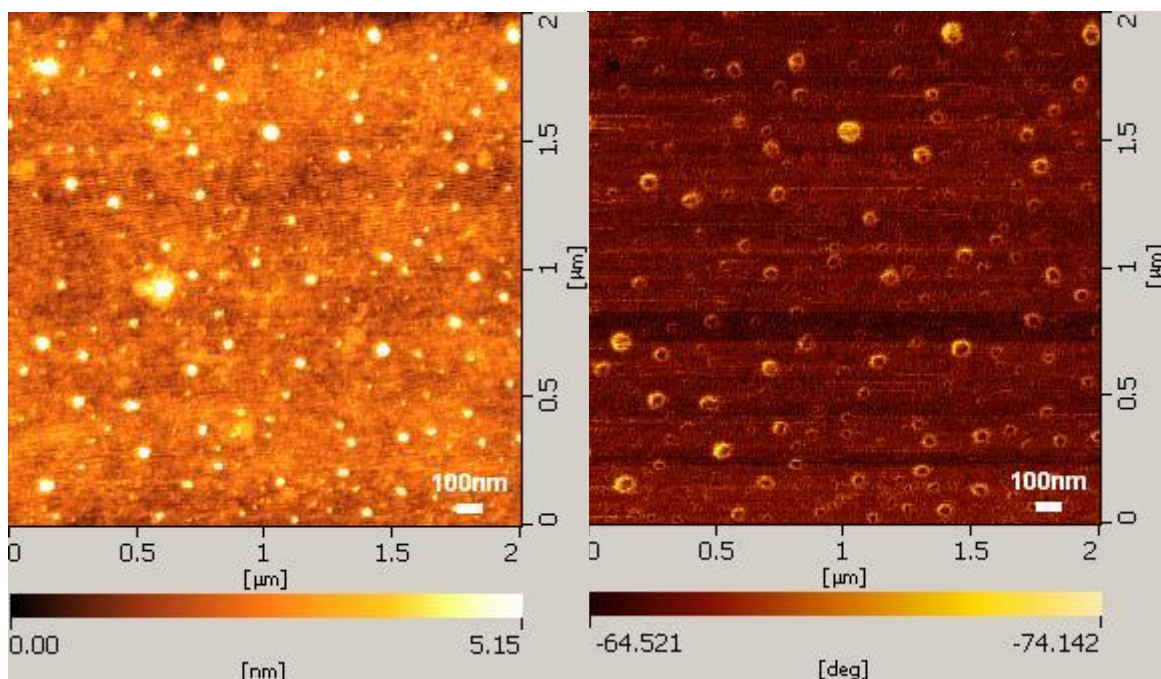


Figure S7. AFM image of GLBT₁₉₈-*b*-SPE₈₁₁ (50 mg/mL) on a glass substrate (left: height mode, flattened, right: phase mode).

The AFM measurement was carried out under the following condition: A Seiko SPI3800 probe station and SPI300 unit system in dynamic force mode (non-contact mode) were operated with microcantilevers. (OMCL-AC240TS-C3, Olympus, typical resonance frequency: 70 kHz and typical spring constant: 1.7 N/m) For sample preparation, aqueous suspensions of colloidal PGLBT-*b*-PSPE particles were dropcast onto a microscope slide glass (IWAKI, Japan) and dried at room temperature more than three days.

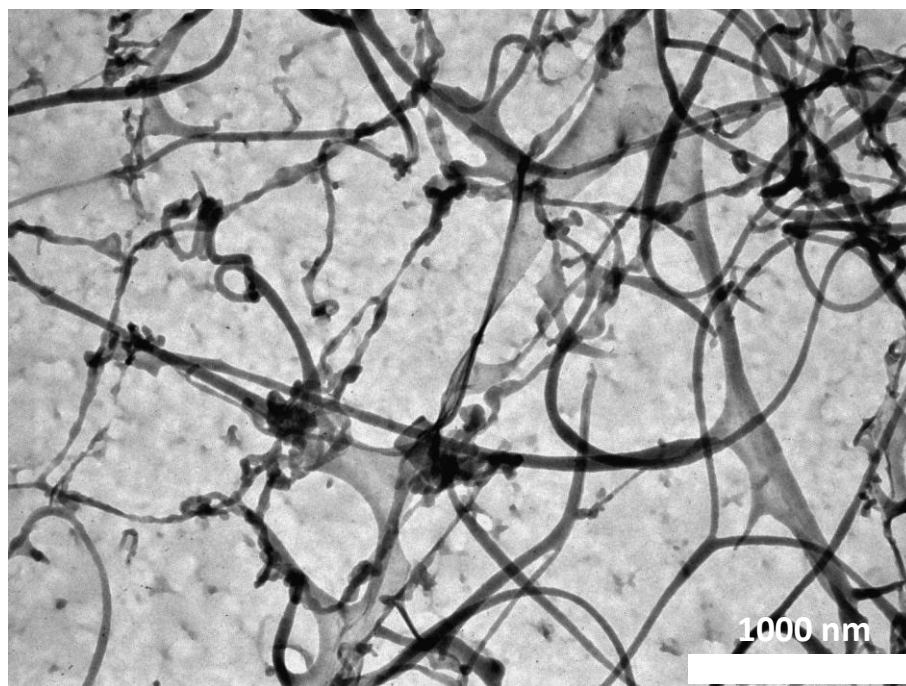


Figure S8. TEM image of GLBT₉₉-*b*-SPE₆₃₀ obtained from the solution in the self-assembled state (conc. = 5 mg/mL)