	Experiment title: **SAXS studies of a thermo-responsive diblcok copolymer: the worm-to-sphere transition**	**Experiment number**: SC-3585
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Report:

We recently reported the polymerisation-induced self-assembly of AB diblock copolymers to form spheres, worms and vesicles directly in aqueous solution at up to 25 w/v % [1]. This synthetic breakthrough is based on a RAFT aqueous dispersion polymerisation formulation: the hydrophilic 'A' block is poly(glycerol monomethacrylate) [PGMA] and the hydrophobic 'B' block is poly(2-hydroxypropyl methacrylate) [PHPMA]. Structural morphologies of micelles formed by PGMA-PHPMA diblock copolymer have been studied by SAXS in a range of q-values 0.003 - 0.2 Å^{-1} using static measurements and time-resolved measurements for various temperature jump and ramp protocols. Different diblock copolymer chemical compositions (PGMA$_x$-PHPMA$_y$, where x = 54 - 78 and y = 140 - 1000) using a number of concentrations (from 1%wt to 10 wt%) where analysed in these experiments. Highly concentrated as-synthesised copolymer dispersions were diluted from 20 wt% to required concentration before the SAXS measurements.

Table 1. Selected SAXS fitting results for various -PGMA$_{55}$- PHPMA$_{DP}$ vesicle micelles dispersions. D_w is the mean vesicle diameter, v_{PHPMA} is the volume of the hydrophobic PHPMA segment, R is the radius from the centre of the vesicle to the centre of the membrane, σ_R is the R standard deviation, T_m is the membrane core thickness, σ_T is the T_m standard deviation, R_g PGMA is the radius of gyration of the PGMA brush chain, x_{sol} is the solvent (water) content of the membrane, N_{agg} is the molecule aggregation number of the vesicles. X-ray scattering length density of PGMA, PHPMA and water used for the vesicle micelles model are 11.94x10^{10} cm^{-2}, 11.11x10^{10} cm^{-2} and 9.42x10^{10} cm^{-2}, respectively. The volume of a PGMA$_{55}$ chain (v_{PGMA}) was calculated to be 11.2 ± 1.2 nm^3.

PHPMA DP	Dw nm	vPHPMA nm^3	R nm	σ_R nm	Tm / nm	σ_T / nm	Rg PGMA nm	Xsol	Nagg
400	199 ± 4	79.1 ± 8.6	85 ± 2	19 ± 8	20.2 ± 0.03	2.2 ± 0.04	2.18 ± 0.02	0.45 ± 0.01	12851 ± 2240
500	190 ± 2	98.9 ± 10.7	78 ± 1	16 ± 8	24.7 ± 0.03	2.3 ± 0.04	2.30 ± 0.05	0.38 ± 0.02	11876 ± 1881
800	198 ± 3	158.3 ± 17.1	76 ± 1	32 ± 13	37.7 ± 0.06	2.9 ± 0.07	2.03 ± 0.06	0.62 ± 0.01	6704 ± 1132

Vesicle, worm-like and spherical morphologies of micelles were detected by SAXS (Figure 1). The PGMA-PHPMA diblocks with a relatively short PHPMA block, responsible for the surface curvature of the self-assembled structures, form worm-like micelles (Figure 1A-1C) while long PHPMA blocks form vesicles (Figure 1D). It was detected by time-resolved SAXS measurements that the thermo-responsive worm-like micelles (Figure 1A and 1B) demonstrate a fully reversible worm-to-spheres transition upon cooling to 5 °C and heating to 25°C which was also confirmed by thermocycling up to 5 times (Figure 1A). A comprehensive model developed for vesicle [2], worm-like [3] and spherical [4] micelles have been adopted for our SAXS data analysis (Table 1, Figure 1C and 1D). Form factor models based on chemical composition of the diblocks produced resonably good fits to the worms data providing an access to structural information such as contour length of the worms, width, radius, radius of gyration of the corona PGMA block, polydispersity, solvent concentration in the micelles core together with their evolution during the temperasture treatments (Figure 1C). A similarly good fit to the data was obtained for vecsicle micelles (Figure 1D and Table 1). A power law relation between membrane thickness and degree of polymerization (DP) of PHPMA block was established (Figure 2). We are currently in a preparation of manuscripts assosiated with the results obtained in these experiments.

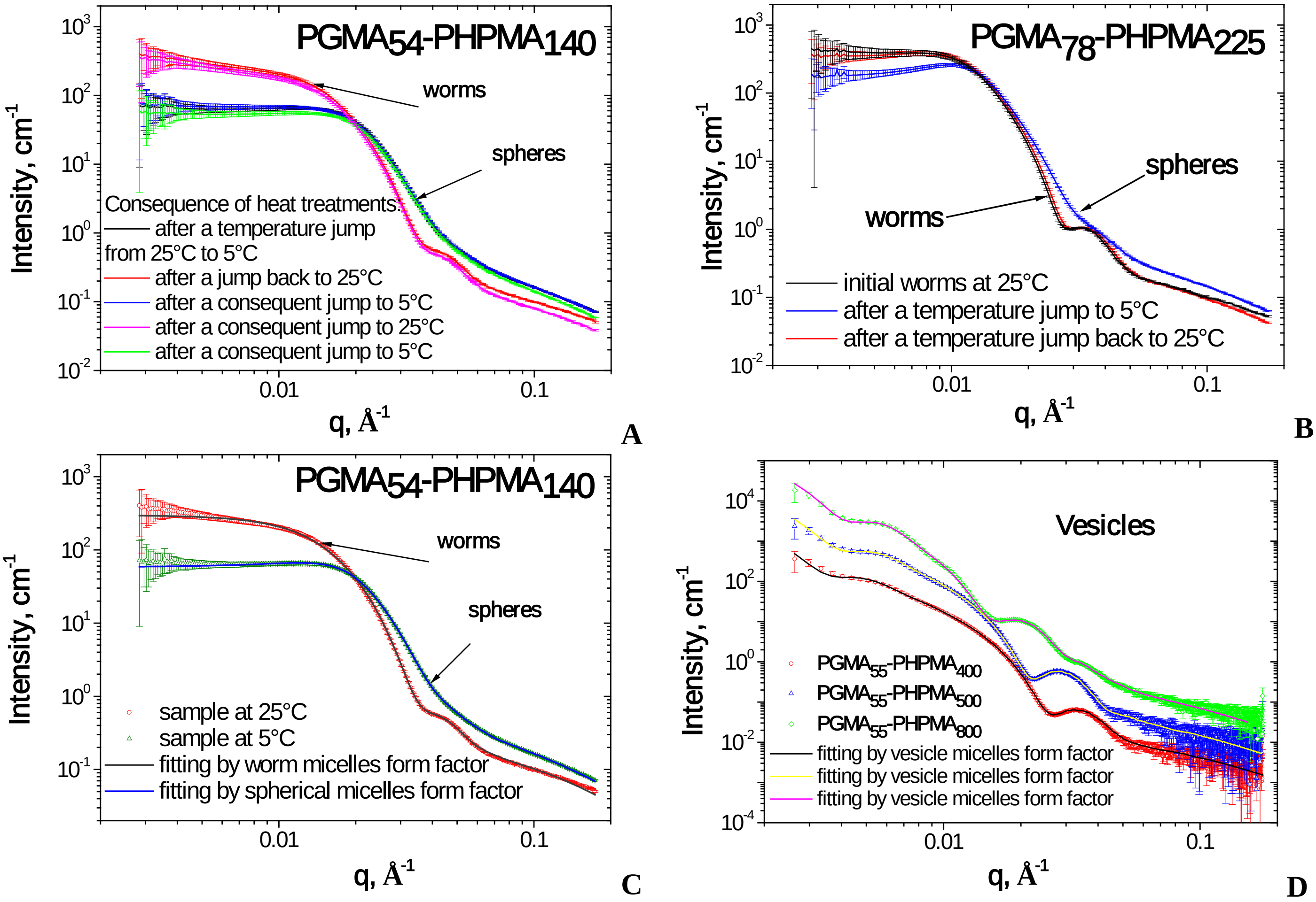

Figure 1. SAXS results for time-resolved worm-to-sphere transitions (A and B) and fitted data for spherical, worm-like (C) and vesicle (D) micelles. Parameters of the fittings presented on the graph for the worms (R_c = 76 Å, R_g = 18 Å, core solvent concentration = 0.2, worm contour length = 5000 Å, worm Kuhn length = 72 Å) and the spheres (R_c = 84 Å, R_g = 18 Å, core solvent concentration = 0.4). Structure factors were counted in the fitting models. Vesicle fitting parameters are given in Table 1.

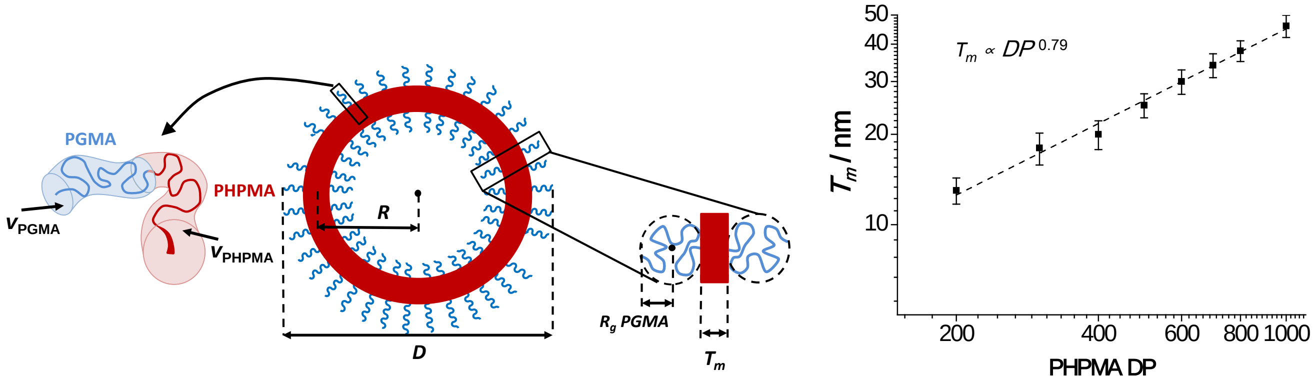

Figure 2. Structural model for vecicle micelles explained and evolution of membrane thickness (T_m) with PHPMA DP for a series of $PGMA_{55}$- $PHPMA_{DP}$ block-copolymer vesicles as measured by SAXS.

Reference:

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2. Bang, J; Jain, SM; Li, ZB; et al., *Macromolecules*, **2006**, *39*, 1199-1208.
3. V. M. Garamus, J. S. Pedersen et al., *Langmuir*, **2000**, *16*, 6431-6437.
4. J. S. Pedersen, *Journal of Chemical Physics*, **2001,** *114*, 2839-2846.