

Supplementary information for:

**Self-assembly of double hydrophobic block copolymers in water-ethanol mixtures:
From micelles to thermo-responsive micellar gels**

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Materials:

Absolute ethanol was obtained from Biosolve Ltd. and used within one month after opening the bottle to prevent significant water attraction. Demineralized water was used in all experiments. Ethanol-*d*₆ was purchased from Aldrich. PMMA-84K ($M_n = 84.2$ kDa; PDI = 1.02) was obtained from PSS.

Instrumentation:

Size exclusion chromatography (SEC) of the PS-*b*-PMMA diblock copolymers was performed on a Shimadzu system with a RID-6A refractive index detector and a PLgel 5 μ m Mixed-D column. A solution of 4% triethylamine and 2% isopropanol in chloroform was used as eluent at a flow rate of 1 mL/min and a column temperature of 50 °C. Molecular weights were calculated against polystyrene standards. SEC of PMMA was performed on a Shimadzu system equipped with a SCL 10A system controller, a LC-10AD pump, a RID-10A refractive index detector, a SPD-10A UV detector and both a PSS Gram30 and a PSS Gram1000 column in series, whereby *N,N*-dimethylacetamide with 5 mmol LiCl was used as eluent at 1 mL/min flow rate and the column oven was set to 60 °C. The molecular weights were calculated using poly(methyl methacrylate) standards.

$^1\text{H-NMR}$ spectra were recorded on a Varian Gemini 400 MHz spectrometer at room temperature using deuterated chloroform (CDCl_3). Chemical shift were calibrated against residual solvent signals.

(Cryo-)Transmission electron microscopy measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB_6 filament). Images were recorded with a bottom mounted $1\text{k} \times 1\text{k}$ Gatan CCD camera. A Gatan cryo-holder operating at $-174\text{ }^\circ\text{C}$ was used for the cryo-TEM measurements. TEM grids, both 200 mesh carbon coated copper grids and R2/2 Quantifoil Jena grids were purchased from SPI. Prior to blotting the grids made hydrophilic by surface plasma treatment using a Cressington 208 carbon coater operating at 5 mA for 40 seconds. For conventional sample preparation $3\text{ }\mu\text{L}$ aliquots were applied to a 200 mesh carbon coated copper grid and subsequently excess liquid was quickly manually blotted away with filter paper. Cryo-TEM specimens were prepared within the environmental chamber ($22\text{ }^\circ\text{C}$, relative humidity 100%) of an automated vitrification robot (FEI Vitrobot Mark III). Excess liquid was blotted away (-2 mm offset, 2 seconds) with filter paper within the environmental chamber of the Vitrobot. The grids were subsequently shot through a shutter into melting ethane placed just outside the environmental chamber. Vitrified specimens were stored under liquid nitrogen before imaging.

The turbidity measurements were performed in the Crystal16 turbidimeter from Avantium Technologies. The transmittance was measured during two controlled heating/cooling cycles from $1\text{ }^\circ\text{C}$ to $75\text{ }^\circ\text{C}$ with a heating rate of $1.0\text{ }^\circ\text{C}$ per minute. The second cycle was used to determine the transition temperatures at 10% transmittance.

SANS Measurements

SANS experiments were conducted on the time-of-flight LOQ diffractometer at the ISIS neutron facility. The incident wavelength range of 2.2 to 10 \AA gave rise to a Q-range of 0.009 to 0.249 \AA^{-1} .¹ Absolute intensities for $I(Q)$ (cm^{-1}) were determined within 5% by measuring the scattering from a partially deuterated polymer standard. Standard procedures for data treatment were employed.¹ Measurements were performed in a 5 mm quartz cell using sample concentrations of 5 mg/mL in ethanol- d_6 / D_2O (80/20 wt%) for PMMA-14K and PMMA-27K or 3 mg/mL for PMMA-84K. The solutions were filtrated over 200 nm filters before the measurements. The measurements were performed at $20\text{ }^\circ\text{C}$ except for PMMA-84K, which was measured at $40\text{ }^\circ\text{C}$ to ensure full solubility of the polymer. Solvent-scattering profiles were subtracted for background correction.

The SANS data were mathematically modelled using the multi-model FISH analysis program to determine the radii of gyration and the chain conformation.² This program is based on an iterative least-squares algorithm and allows for many common scattering laws to be tested. The models used were not chosen randomly; the general form factors of the scattering curves and the chemical knowledge of the

systems were taken into account. It was found that the systems under study in this investigation were described well by both a Gaussian coil and ellipsoid model. Absolute intensity and scale factor checks were determined for each data set to ensure that the most suitable structural model had been chosen and in all cases the Gaussian Coil model proved to be the most suitable form factor for describing the chain conformation. Values for the absolute scattering intensity, $I(0)$, flat background and radius of gyration are obtained from this model, which were allowed to adjust freely during the modelling process, but not allowed to become physically unrealistic. For the Gaussian coil model, $I(0)$ is given by:

$$I(0) = \phi \Delta\rho^2 V$$

where $\Delta\rho$ the scattering length density difference between the polymer and the solvent, ϕ = concentration of polymer (in $\text{g}\cdot\text{cm}^{-3}$) / density (in $\text{g}\cdot\text{cm}^{-3}$) and V is the volume of polymer in one scattering object (the coil), and is given by:

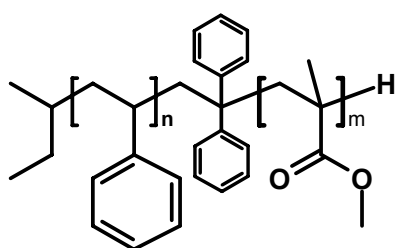
$$V = \frac{M_n}{d \cdot N_A}$$

here M_n is the molecular weight of the polymer (in $\text{g}\cdot\text{mol}^{-1}$), d the density and N_A is Avogadro's constant.

Further detail on the models used can be found in the FISH manual which can be downloaded from:

<http://www.small-angle.ac.uk/small-angle/Software.html>.

PS-*b*-PMMA block copolymer synthesis



The poly(styrene)-*block*-poly(methyl methacrylate) block copolymers investigated in this work were prepared by anionic polymerization following a previously reported synthetic method.³ The anionic polymerization of styrene was performed at 50 °C in cyclohexane using *s*-butyllithium as initiator. Subsequently, diphenylethylene was added to reduce the reactivity of the living anionic chain ends. In the next step, tetrahydrofuran and methyl methacrylate were added and the polymerization was continued at –

75 °C. The polymerization was quenched by the addition of methanol. Purification of the block copolymers was performed by precipitation in methanol.

The resulting polymers showed mono-modal molecular weight distributions as revealed by SEC. ¹H-NMR spectroscopy in combination with SEC measurements were utilized for calculating the chain lengths and composition of the different block copolymers.

PS-*b*-PMMA-I:

First block: $M_{n,PS,SEC}$: 8.8 kDa; $PDI_{PS,SEC}$: 1.08.

Block copolymer: $M_{n,SEC}$ = 13.9 kDa; PDI_{SEC} = 1.16.

¹H NMR spectroscopy: $DP_{styrene}$ = 88 (from SEC); DP_{MMA} = 80.

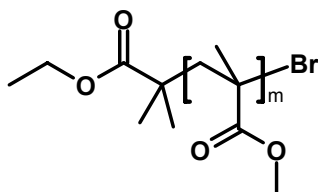
PS-*b*-PMMA-II:

First block: $M_{n,PS,SEC}$: 11.7 kDa; $PDI_{PS,SEC}$: 1.17.

Block copolymer: $M_{n,SEC}$ = 291.2 kDa; PDI_{SEC} = 1.23.

¹H NMR spectroscopy: $DP_{styrene}$ = 112 (from SEC); DP_{MMA} = 2800.

PMMA synthesis



The PMMA-14K and PMMA-27K were prepared by atom transfer radical polymerization following a previously reported synthetic method using copper(II) bromide and *N, N, N', N'', N''', N''''*-hexaoligo-(ethyleneglycol) triethylenetetramine (HOEGTETA) as catalytic system, ethyl 2-bromoisobutyrate as initiator and anisole as solvent at 90 °C.⁴ After the polymerization, the polymer was passed over a neutral aluminum oxide column to remove the copper catalyst followed by precipitation in methanol to remove residual monomer.

The resulting polymers showed mono-modal molecular weight distributions as revealed by SEC.

PMMA-14K: M_n = 13.8 kDa; PDI = 1.18.

PMMA-27K: M_n = 27.4 kDa; PDI = 1.43.

Micellization procedure

The required amount of PS-*b*-PMMA block copolymer was weighed into a HPLC vial (2.0 mL) covered with a screw cap containing a hole and a septum. The appropriate amount of the ethanol-water (80/20 wt%) solvent mixture was added to obtain the desired concentration. Subsequently, this mixture of solid polymer and solvent was heated with a heat gun until a slight overpressure was noticed by expansion of the septum. The micellar solutions and gels were obtained by cooling to ambient temperature.

CAUTION: Always use high quality HPLC vials covered with a screw cap with a hole and a septum, which acts as pressure valve, to prevent too high overpressures potentially leading to explosion of the vial.

References:

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- (3) Guerrero-Sanchez, C.; Abeln, C.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4151-4160.
- (4) Becer, C. R.; Hoogenboom, R.; Fournier, D.; Schubert, U. S. *Macromol. Rapid Commun.* **2007**, *28*, 1161-1166.