

Supporting information for:

The effects of molecular weight dispersity on block copolymer self-assembly

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1. Experimental section

1.1 Materials

The monomers Styrene and hydroxyl ethyl acrylate were de inhibited over a column of activated basic alumina before use. 2-(Dodecylthiocarbonothioylthio)propionic acid (DOPAT) was synthesized according to the literature¹. The reagents and chemicals that were used for the synthesis of DOPAT were purchased from Sigma-Aldrich or VWR. 1,1'- Azobis(isobutyronitrile) (AIBN 98% Sigma-Aldrich) was recrystallized twice from methanol before use. All solvents were used as received (99% Chem-Supply).

1.2 Characterization

Analytic methods

GPC

Analysis of the polymers was performed on a PSS SECcurity2GPC system operated by PSS WinGPC software, equipped with a SDV 5.0 μm guard column (50 x 8 mm), followed by three SDV analytical 5.0 μm columns with varying porosity (1000 Å, 100000 Å and 1000000 Å) (50 x 8 mm) and a differential refractive index detector using tetrahydrofuran (THF, RCI Labscan, 99.9%) as the eluent at 40 °C with a flow rate of 1 mL·min⁻¹. Online SEC is performed on a PSS instrument fitted with a PSS SDV analytical column of 3.0 μm particles with a porosity of 1000 Å and an evaporative light scattering detector (ELSD) ELS1300 using tetrahydrofuran (THF) as the eluent at 40 °C with a flow rate of 1 mL min⁻¹. The SEC system was calibrated using linear molecular weight polystyrene standards ranging from 474–60 000 Da.

NMR

Proton nuclear magnetic resonance (¹H-NMR) was undertaken using a Bruker Avance III 400 which operated at 400 MHz, using deuterated solvents in the form of chloroform (CDCl₃)

Small-Angle Neutron Scattering (SANS)

SANS measurements were undertaken on the Bilby instrument^{2,3} at the Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Heights, NSW, Australia. Samples were prepared using D₂O as the aqueous phase and measured at a concentration of 1 mg·mL⁻¹ for 2 hours at room temperature in 1 mm path-length quartz window cells. Raw scattering data from the samples, empty cell and D₂O+THF background have been reduced following standard instrument procedure. SANS data were modeled using the SasView software (<http://www.sasview.org>) and analysed using the sphere, cylinder and ellipse models presented by Guinier and Fournet.⁴ Pair distribution function $p(r)$ have been calculated using GNOM software, which is a part of the ATSAS suit.⁵

STEM

All Scanning Transmission Electron Microscopy (STEM) images were taken on the Magellan 400 FEGSEM. The Magellan 400 FEGSEM is an extreme high resolution (XHR) instrument equipped with a monochromator allowing improved resolution at low accelerating voltages. This system is fitted with a multi-sample holding station allowing for analysing multiple samples at once without compromising the vacuum. For STEM a special STEM detector is used with the system. The system consists of a FEG; 5-axis piezo stage; IR chamber camera; oil-free pumping system; retractable DBS annular BSE detector; retractable STEM3 detector; quick loader; beam deceleration; in-lens detectors; NavCam; plasma cleaner; cryo-trap; Bruker Quantax 400 X-ray analysis system and 30mm² SDD with super light element window (slew).

3. Results

3.1 Polymerizations

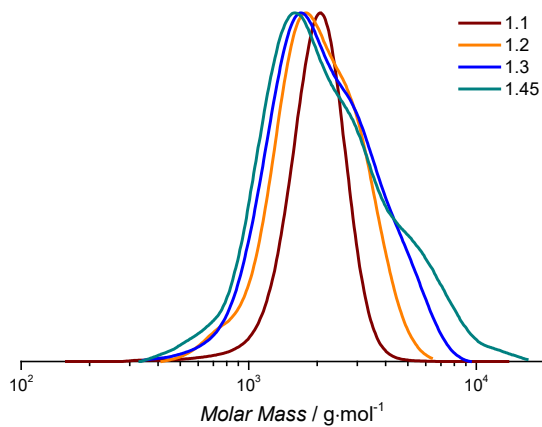


Figure S1. Molecular weight distributions of P(styrene) at DP 15 with different dispersities.

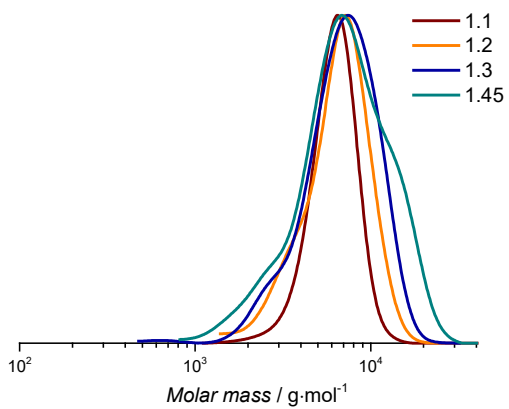


Figure S2. Molecular weight distributions of P(styrene) at DP 50 with different dispersities.

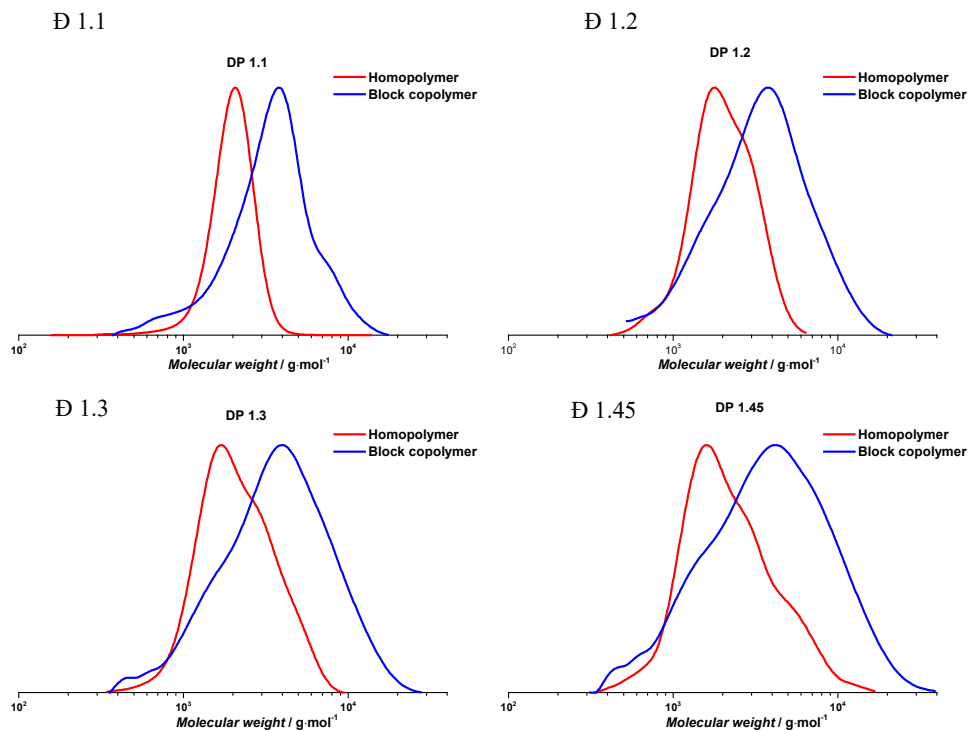


Figure S3. Molecular weight of block copolymers made from a DP 15 styrene homoblock.

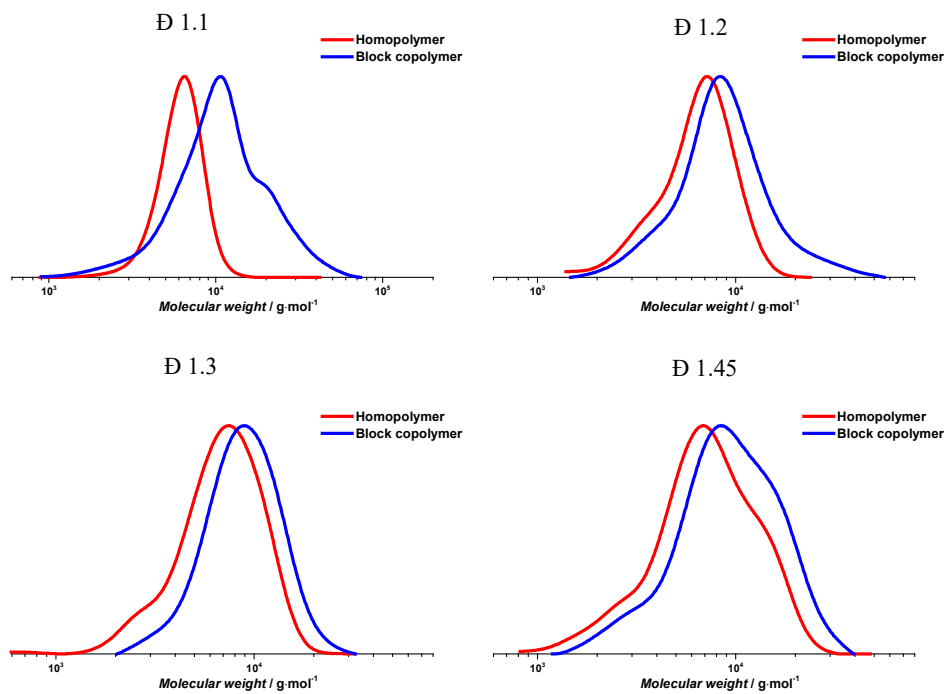


Figure S4. Molecular weight distributions of block copolymers made from a DP 50 Styrene homoblock.

Table S1 DP_n shows the degree of polymerisation (block length) as calculated via ¹H NMR measurements. M_n shows the number average molecular weight M_p the molecular weight of the highest peak and Đ represent the dispersity of the molecular weight where Đ₁ denotes the dispersity of the first block, Đ₂ the dispersity of the complete BCP.

Sample	DP _n	M _n g·mol ⁻¹	M _p g·mol ⁻¹	Đ ₁	Sample	DP _n	M _n g·mol ⁻¹	M _p g·mol ⁻¹	Đ ₂
DP 15 Homopolymer 1.1	15	1800	1800	1.10	DP 15 BCP 1.1	15	2700	3780	1.50
DP 15 Homopolymer 1.2	15	1800	1750	1.2	DP 15 BCP 1.2	15	2650	3600	1.56
DP 15 Homopolymer 1.3	15	1800	1600	1.3	DP 15 BCP 1.3	15	2600	3800	1.75
DP 15 Homopolymer 1.45	15	1800	1500	1.45	DP 15 BCP 1.45	15	2500	3920	2.0
DP 50 Homopolymer 1.1	50	5700	6400	1.1	DP 50 BCP 1.1	50	8500	10500	1.53
DP 50 Homopolymer 1.2	50	5600	7100	1.2	DP 50 BCP 1.2	50	7500	8500	1.36
DP 50 Homopolymer 1.3	50	5700	7200	1.3	DP 50 BCP 1.3	50	8000	9000	1.2
DP 50 Homopolymer 1.45	50	5650	6750	1.45	DP 50 BCP 1.45	50	7500	8300	1.45

3.2 Dynamic light scattering

Table S2 Dynamic light scattering results for BCPs with different dispersity core-forming blocks.

Sample	Intensity average (nm)	Volume average (nm)	Number average (nm)	PDI
DP 15 BCP 1.1	130	115	100	0.118
DP 15 BCP 1.2	140	55	35	0.185
DP 15 BCP 1.3	155	85	60	0.200
DP 15 BCP 1.45	120	70	50	0.150
DP 50 BCP 1.1	118	60	40	0.170
DP 50 BCP 1.2	110	60	40	0.150
DP 50 BCP 1.3	110	83	60	0.160
DP 50 BCP 1.45	85	45	30	0.150

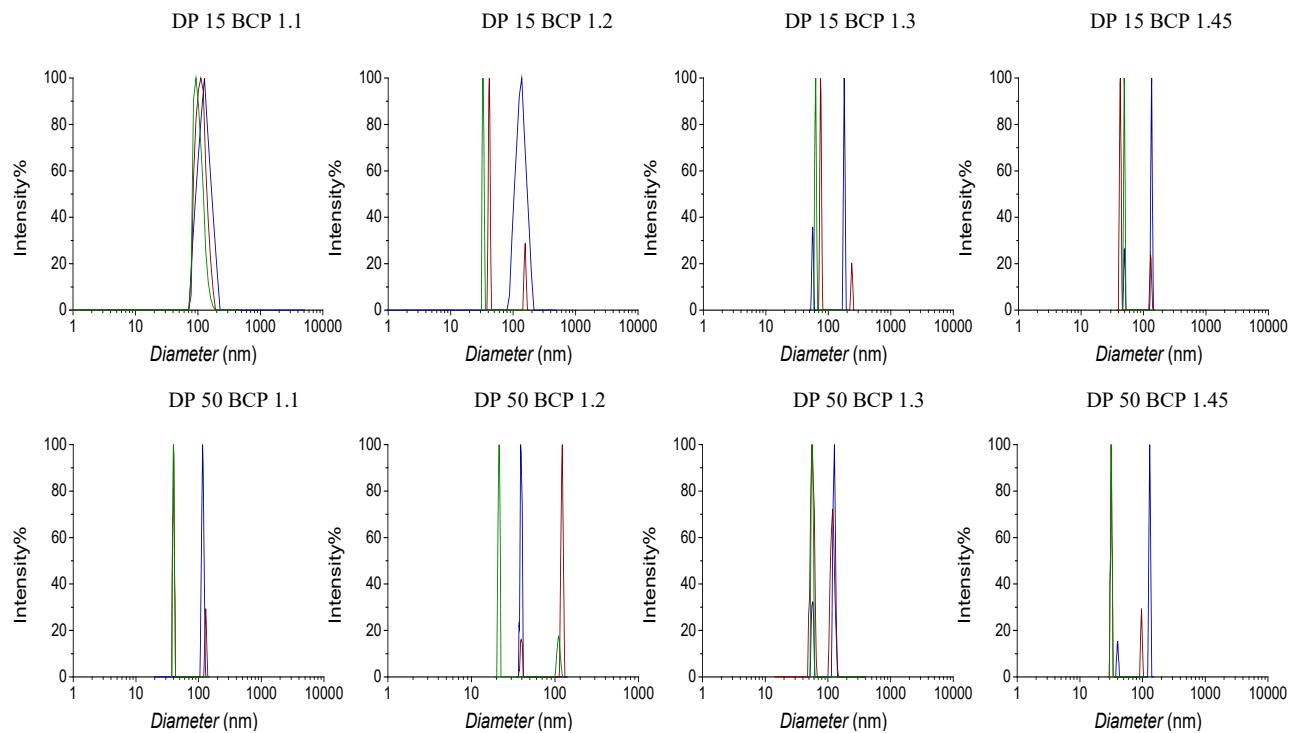


Figure S5. Dynamic light scattering results for BCPs with different dispersity core forming blocks. Showing the intensity (blue) number (green) and volume (red) distributions.

3.3 Small Angle Neutron Scattering

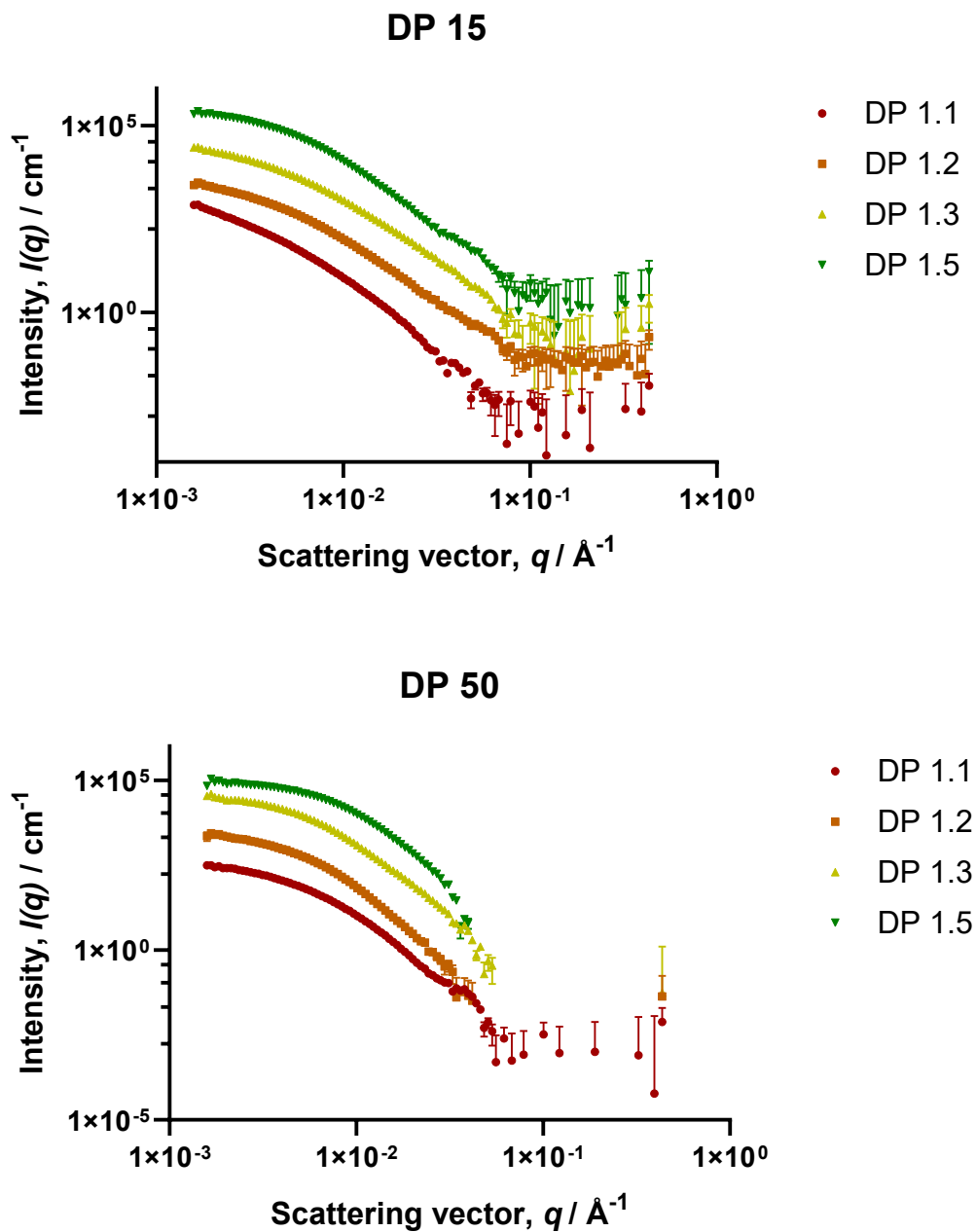


Figure S6. Small-angle neutron scattering data from PHEA-b-PS with a D₂O background subtracted.

3.4 GNOM/ATSAS suite

Scattering intensity for diluted solution of particles with maximum dimension D_{max} can be expressed as follows:

$$I(Q) = 4\pi \int_0^{D_{max}} p(r) \frac{\sin Qr}{Qr} dr \quad (1)$$

Where the distribution of interatomic distances, $p(r)$, is calculated as $p(r) = \gamma(r) \cdot r^2$ where $\gamma(r)$ is a spherically averaged autocorrelation function of the excess scattering density. The distribution becomes zero at $r = 0$ and $r = D_{max}$.

$$p(r) = \frac{r^2}{2\pi^2} \int_0^\infty Q^2 I(Q) \frac{\sin Qr}{Qr} dQ \quad (2)$$

The algorithm allows to calculate $p(r)$ providing it with D_{max} value as an input. To properly analyze $p(r)$, several conditions need to be confirmed. First, the density distribution inside the particles has to be considered as uniform. Second, the samples must be dilute, so there is no influence of the structural factor on the scattering intensity. When these conditions are met a common approach is to access $p(r)$ of an individual species in monodisperse solutions. For the case of polydisperse samples $p(r)$ yields information about averaged properties of the entire ensemble.

3.4 Electron Microscopy

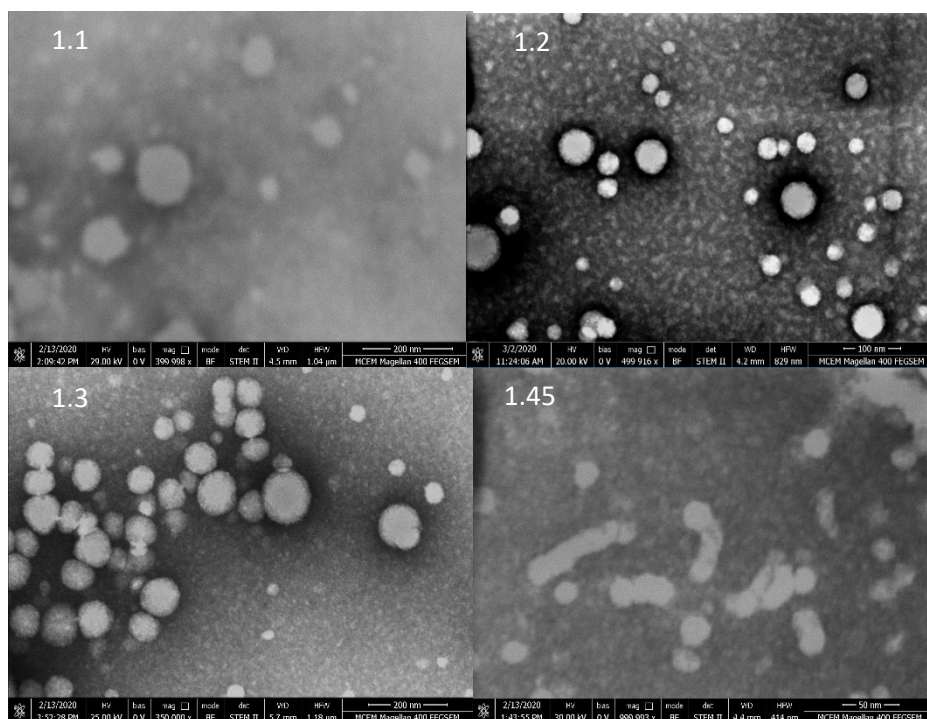


Figure S7. STEM images of particles made with DP 15 samples and different dispersity. It should be noted that elongated ensembles observed in image 1.45 are the consequence of particles sticking together during sample preparation.

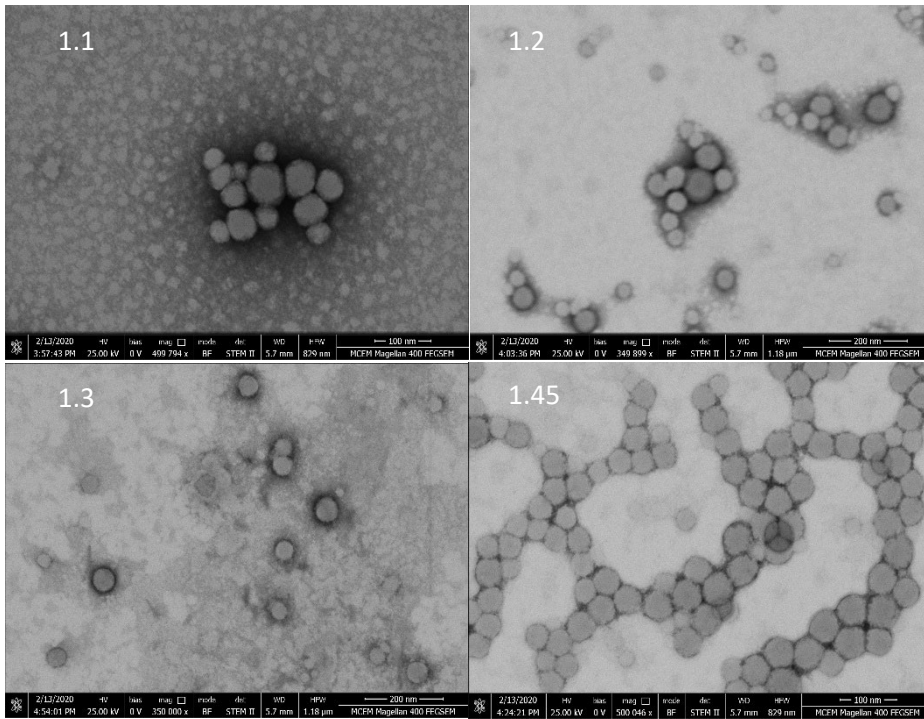


Figure S8. STEM images of particles made with DP 50 samples and different dispersity.

4. References

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2. A. Sokolova, J. Christoforidis, A. Eltobaji, J. Barnes, F. Darmann, A. E. Whitten and L. de Campo, *Neutron News*, 2016, **27**, 9-13.
3. A. Sokolova, A. E. Whitten, L. de Campo, J. Christoforidis, A. Eltobaji, J. Barnes, F. Darmann and A. Berry, *Journal of Applied Crystallography*, 2019, **52**, 1-12.
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5. K. Manalastas-Cantos, P. Konarev, N. Hajizadeh, A. Kikhney, M. Petoukhov, D. Molodenskiy, A. Panjkovich, H. Mertens, A. Gruzinov, C. Borges, C. Jeffries, D. Svergun and D. Franke, *Journal of Applied Crystallography*, 2021, **54**, 343-355.