Supporting Information for:

Time-resolved small-angle neutron scattering studies of the thermally-induced exchange of copolymer chains between spherical diblock copolymer nanoparticles prepared via polymerization-induced self-assembly

Erik J. Cornel,[1] Gregory N. Smith,[1,2] Sarah E. Rogers,[3] James E. Hallett,[4] David J. Growney,[5] Timothy Smith,[5] Paul S. O'Hora,[5] Sandra van Meurs,[1] Oleksandr O. Mykhaylyk[1,] and Steven P. Armes[1,*]*

1. Dainton Building, Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire S3 7HF, UK.

2. Niels Bohr Institute, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

3. Rutherford Appleton Laboratory, Harwell Oxford, Didcot OX11 0QX, UK.

4. H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK.

5. Lubrizol Ltd, Nether Lane, Hazelwood, Derbyshire, DE56 4AN, UK.

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1. NMR data analysis of PLMA macro-CTA, PLMA-PMMA and PLMA-d$_8$PMMA
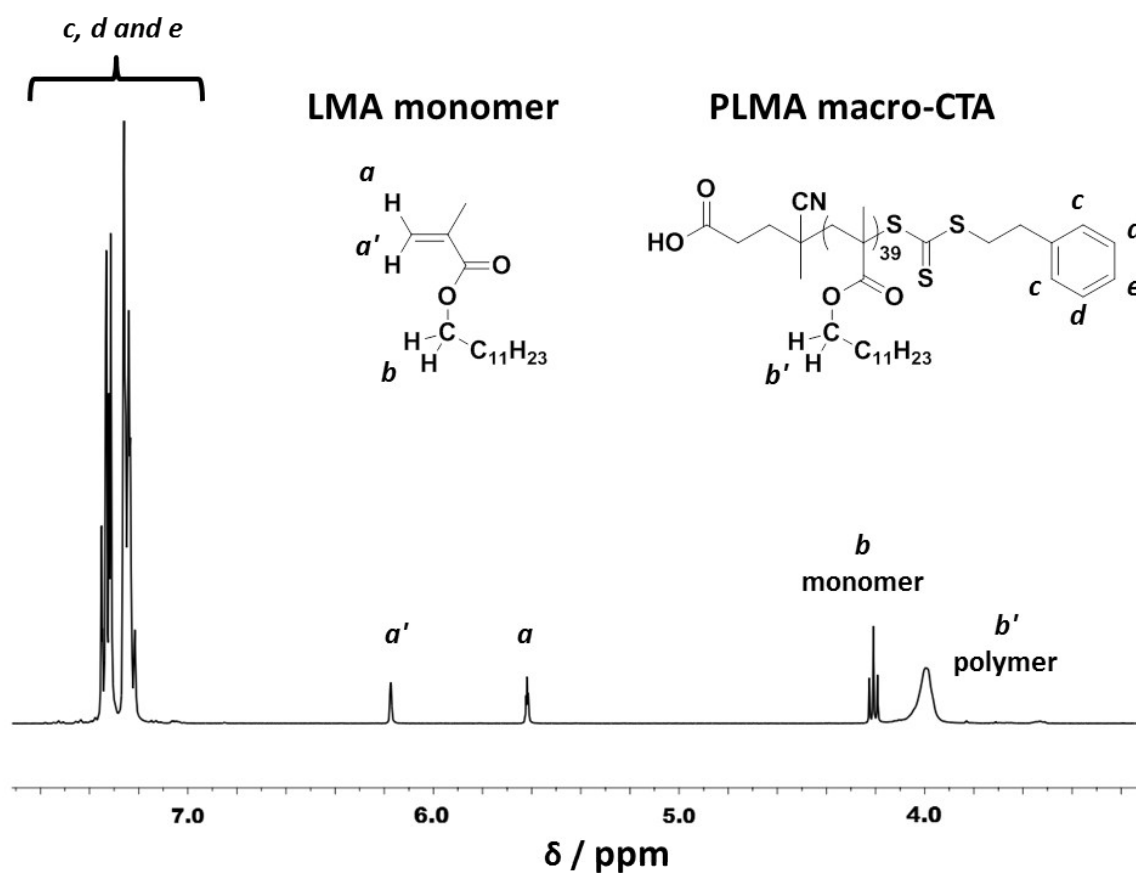
Figure S1. Representative proton NMR spectrum recorded in CDCl$_3$ for a sample of the reaction solution taken during the RAFT-mediated solution polymerization of lauryl methacrylate. After a reaction time of 4 h, a monomer conversion of 76% was calculated using **Equation S1** by comparing the integrated monomer vinyl protons (*a* and *a'*) with the integrated oxymethylene signals (*b*$_{monomer}$ and *b'*$_{polymer}$) assigned to LMA monomer and PLMA homopolymer.

$$LMA\ conversion\ (\%) = \left(1 - \frac{a + a'}{b_{monomer} + b'_{polymer}}\right) \times 100\% \quad (S1)$$

The mean DP of the PLMA precursor was determined *via* end-group analysis by analyzing a proton NMR spectrum recorded for the purified homopolymer in CD_2Cl_2. In this case, the proton signal assigned to the aromatic end-group at 7.18-7.38 ppm was compared to that of the oxymethylene signal of the PLMA homopolymer at 3.92–4.08 ppm ($b'_{polymer}$) (**Equation S2**).

$$DP_{PLMA} = \frac{(c + d + e) \times \frac{2}{5}}{b'_{polymer}} \quad (S2)$$
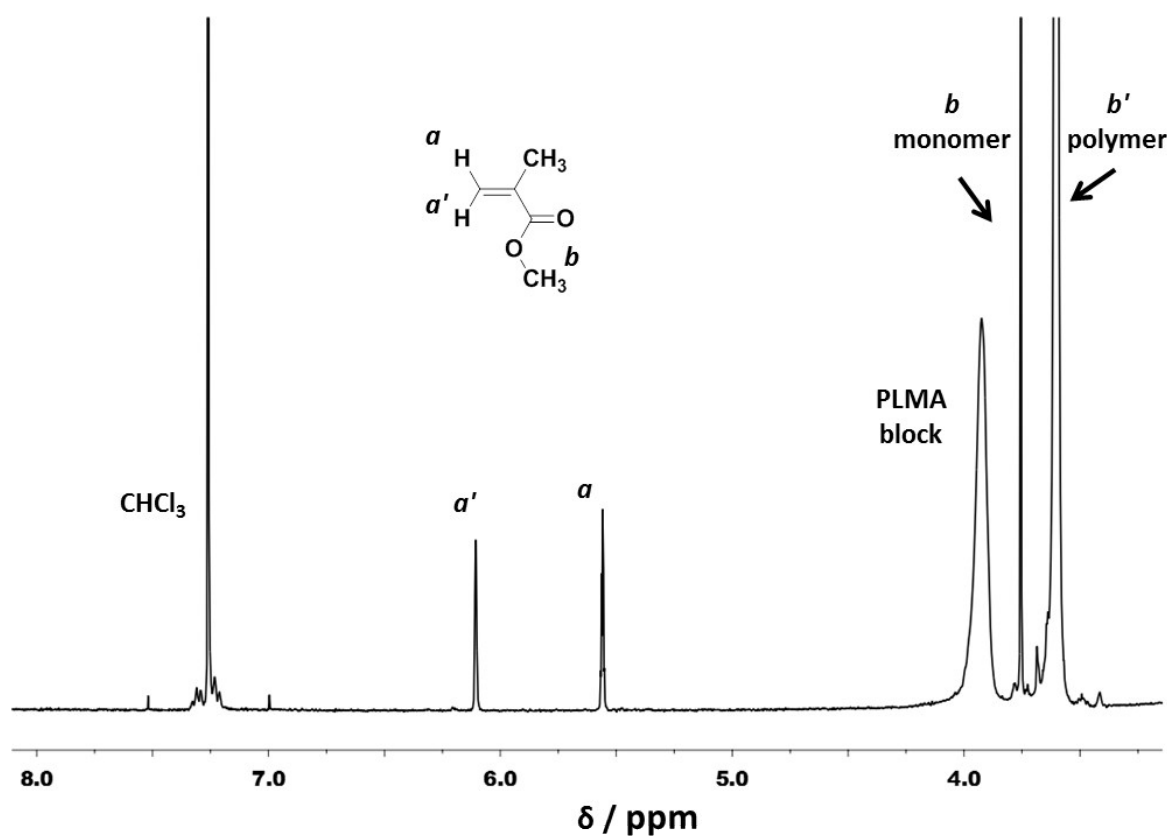
Figure S2. Representative proton NMR spectrum recorded for a crude sample of $PLMA_{39}$-$PMMA_{55}$ (after dilution with $CHCl_3$ to ensure nanoparticle dissolution). Monomer conversions were calculated according to **Equation S3** using the integrated monomer vinyl signals (*a* and *a'*) and the methyl signals ($b_{monomer}$ and $b'_{polymer}$) assigned to the MMA and PMMA.
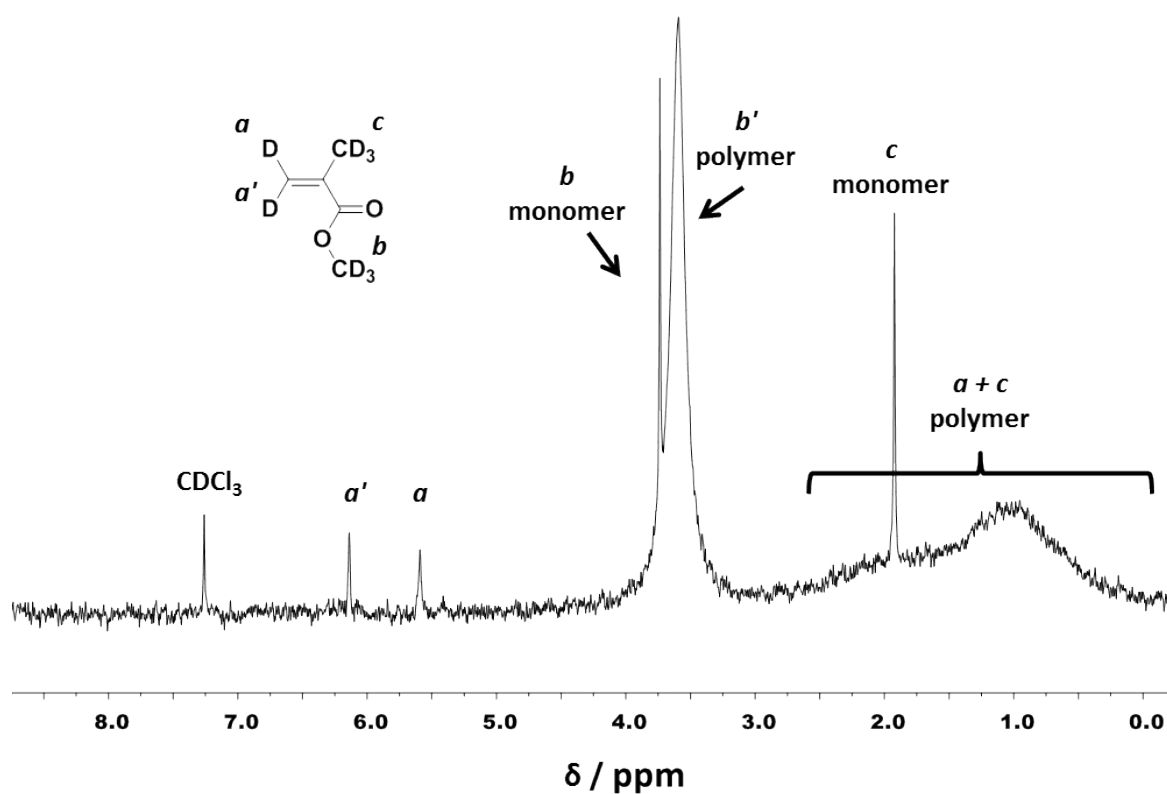
Figure S3. Representative deuterium NMR spectrum recorded for a sample of the crude reaction solution during the synthesis of PLMA$_{39}$-d$_8$PMMA$_{57}$ (after dilution with CHCl$_3$ to ensure nanoparticle dissolution). Monomer conversions were calculated according to **Equation S3** by comparing the integrated monomer vinyl signals (a and a') with the integrated methoxy signals assigned to MMA and PMMA ($b_{monomer}$ and $b'_{polymer}$).

$$MMA \text{ or } d_8MMA \text{ } conversion \text{ } (\%) = \left[1 - \frac{(a + a') \times \dfrac{3}{2}}{b_{monomer} + b'_{polymer}} \right] \times 100\% \quad (S3)$$

2. Small-angle scattering (SAS) models and parameters

SAS model for molecularly-dissolved PLMA$_{39}$ chains in *n*-dodecane

The differential scattering cross-section per unit sample volume, $\frac{d\Sigma}{d\Omega}(q)$, for dissolved molecules can be expressed as

$$\frac{d\Sigma}{d\Omega}(q) = \varphi(\Delta\xi)^2 V_c F_c(q, R_g) \quad (S4)$$

where φ is the molecule volume fraction in the solution, $\Delta\xi$ is the excess scattering length density of the molecules in the solution calculated as a difference between the scattering length density of the molecule (ξ_c) and the solvent (ξ_{sol}), V_c is the total molecular volume and $F_c(q, R_g)$ is the form factor for the molecule. To determine the mean radius of gyration of the polymer coil (R_g), the SAXS pattern recorded for molecularly-dissolved PLMA$_{39}$ chains (or unimers) in *n*-dodecane was fitted using the following form factor expressed as the Debye function[1]:

$$F_c(q, R_g) = \frac{2\left[\exp\left(-q^2 R_g{}^2\right) - 1 + q^2 R_g{}^2\right]}{q^4 R_g{}^4} \quad (S5)$$

SAS model for dilute PLMA$_{39}$–PMMA$_x$ and PLMA$_{39}$–d$_8$PMMA$_x$ spheres

In general, the differential scattering cross-section per unit sample volume $\frac{d\Sigma}{d\Omega}(q)$ for a dispersion of particles can be expressed as:

$$\frac{d\Sigma}{d\Omega}(q) = N S_{SF}(q) \int_0^\infty \dots \int_0^\infty F(q, r_1, \dots, r_k) \Psi(r_1, \dots, r_k) dr_1 \dots dr_k \quad (S6)$$

where $S_{SF}(q)$ is the structure factor. This factor describes variations of scattering from randomly arranged particles, which become more pronounced when considering either strongly interacting scattering objects or densely-packed concentrated dispersions. Since only dilute dispersions are considered in this study, $S_{SF}(q) = 1$. $F(q, r_1, \dots, r_k)$ is a particle form factor expressed in terms of a set of k parameters, $\Psi(r_1, \dots, r_k)$ is the parameter distribution function and *N* is the particle number density per unit sample volume, which is expressed as:

$$N = \frac{\varphi}{\int\limits_0^\infty ... \int\limits_0^\infty V(r_1,...,r_k)\Psi(r_1,...,r_k)dr_1...dr_k} \quad (S7)$$

where $V(r_1,...,r_k)$ is the particle volume and φ is the particle volume fraction in the dispersion. For spherical micelles, it is sufficient to consider only the polydispersity of the micelle core radius, defined as r_1, which is assumed in the present study to be a Gaussian distribution:

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

where R_s is the mean micelle core radius and σ_{Rs} is its standard deviation. All other fitting parameters describing this spherical micelle structural model were considered to be monodisperse (i.e. their distribution functions correspond to Dirac's delta function).

The spherical micelle form factor (**Equation S6**) can be expressed as:[2]

$$F(q,r_1)$$
$$= N_s^2(r_1)\beta_s^2 A_s^2(q,r_1) + N_s(r_1)\beta_c^2 F_c(q,R_g) \qquad + N_s(r_1)[N_s(r_1)$$
$$2N_s^2(r_1)\beta_s\beta_c A_s(q,r_1)A_c(q,r_1) \quad (S9)$$

where $N_s(r_1)$ is the aggregation number (or total number of copolymer chains per spherical nanoparticle):

$$N_s(r_1) = (1 - x_{sol})\frac{\frac{4}{3}\pi r_1^3}{V_s} \quad (S10)$$

where x_{sol} is the fraction of solvent in the micelle core and V_s is the volume of a single core-forming block (**Table S1**).

β_s and β_c represent the total excess scattering of the core-forming block (PMMA or d$_8$PMMA) and the corona-forming block (PLMA), respectively. These values can be calculated by $\beta_s = V_s(\xi_s - \xi_{solv})$ and $\beta_c = V_c(\xi_c - \xi_{solv})$, where V_c is the volume of a single corona-forming block (**Table S1**); ξ_s, ξ_c and ξ_{solv} are the SLDs of the core, corona and solvent (see **Table S1** for the calculated neutron and X-ray SLDs of each component in the dispersion). The self-correlation term for the spherical core in **Equation S8** is expressed as:

$$A_s(q,r_1) = \Phi(qr_1)exp\left(-\frac{q^2\sigma^2}{2}\right) \quad (S11)$$

where

$$\Phi(qr_1) = \frac{3[\sin(qr_1) - qr_1 cos(qr_1)]}{(qr_1)^3} \quad (S12)$$

A sigmoidal interface between the micelle core and corona was assumed for the micelle model (**Equation S10**). This is described by the exponent term with a width σ accounting for a decaying scattering length density at the membrane surface. This σ value was fixed at 0.22 nm during fitting. The self-correlation term for the corona block, $F_c(q)$, is given by the Debye function (**Equation S5**). The scattering amplitude of the corona self-term (**Equation S9**) was obtained from a normalized Fourier transform of the radial density distribution function of the coronal chains in the micelles:

$$A_c(q,r_1) = \frac{\int_{r_1}^{r_1+2s} \mu_c(r)\frac{sin(qr)}{qr}r^2 dr}{\int_{r_1}^{r_1+2s} \mu_c(r)r^2 dr} exp\left(-\frac{q^2\sigma^2}{2}\right) \quad (S13)$$

The radial profile, $\mu_c(r)$, is expressed by a linear combination of two cubic b splines, with two fitting parameters s and a corresponding to the width of the scattering length density corona profile and the function weight coefficient, respectively. This information can be found elsewhere,[3, 4] as can the approximate integrated form of **Equation S13**.

According to **Equation S7** the number density per unit sample volume for the spherical micelles can be expressed as:

$$N = \frac{\varphi}{\int_0^\infty V(r_1)\Psi(r_1)dr_1} \quad (S14)$$

where $V(r_1)$ is the total volume of copolymer in a spherical micelle $[V(r_1) = (V_s + V_c)N_s(r_1)]$.

SAS model parameters (copolymer block volumes and SLDs)

The molecular volume of each copolymer block, i.e. $PLMA_{39}$, $PMMA_x$ and d_8-$PMMA_x$, (**Table S1**) were calculated from:

$$V_b = DP \cdot v_m \quad (S15)$$

where DP is the degree of polymerization and v_m is the volume of the repeat unit in each block such that $v_m = \dfrac{M_{Mon}}{N_A \rho}$, where M_{Mon} is the molecular weight of the corresponding block repeat unit, N_A is Avogadro's number and ρ is the mass density of either the core-forming or corona-forming block.

Scattering length densities (SLD) for each component of the nanoparticle dispersion were calculated for neutrons and X-rays (**Table S1**) using:

$$\xi = \frac{\sum_{i=1}^{L} n_i b_i}{v_m} \quad (S16)$$

where L is the number of types of chemical elements in a compound, n_i is the number of atoms of the ith chemical element (or one of its isotopes), b_i is the scattering length of the ith chemical element nucleus (for neutrons) or atom (for X-rays, determined by its number of electrons multiplied by scattering length of an electron), and v_m is the molecular volume of either a single monomer repeat unit or a solvent molecule.

Table S1. Summary of the core- and corona-forming copolymer block volumes (V_s and V_c; expressed in cubic angstroms), mass densities (ρ), and calculated X-ray and neutron SLDs (ξ) for each methacrylic block and also for the various solvent compositions used in this study. Neutron SLDs at 150 °C were calculated using block densities corrected by the thermal expansion coefficient (TEC) reported for hydrogenous poly(methyl methacrylate).[5] The neutron SLD of each solvent (or binary solvent mixture) was calculated using literature densities determined at 20 °C and 150 °C.[6]

	Block volume / Å³	Density / g cm³	X-ray SLD / × 10⁻⁶ Å⁻²	Neutron SLD / × 10⁻⁶ Å⁻² at 20 °C	Neutron SLD / × 10⁻⁶ Å⁻² at 150 °C
PLMA$_{39}$	17716	0.93	8.81	0.13	0.12
PMMA$_{55}$	7736	1.188	10.87	1.07	1.01
d$_8$PMMA$_{57}$	8216	1.255	10.64	6.87	6.49

PMMA$_{94}$	13209	1.188	10.87	1.07	1.01
d$_8$PMMA$_{96}$	14184	1.255	10.64	6.87	6.49
n-dodecane	-	0.75	7.32	-0.46	-0.40
d$_{26}$-dodecane	-	0.864	-	6.71	5.97
n-dodecane + d$_{26}$-dodecane mixture, 38:62 v/v	-	-	-	3.97	3.55

SAS analysis and results

The SAXS patterns of the PLMA macro CTA were fitted using the Debye function (**Equation S4).** The spherical micelle model (**Equations S5-S13**) was used for analyzing scattering patterns of $PLMA_{39}$–$PMMA_x$ and $PLMA_{39}$–d_8PMMA_x spheres. The calculated block volumes and SLDs for each component of the dilute copolymer dispersions (**Table S1**) were fixed during the fitting. Geometric parameters for the micelles (i.e. the mean core radius and its standard deviation, the R_g of the micelle corona block) and the polymer volume fraction were allowed to vary until the best SAXS data fits were obtained (**Table S2**). These four SAXS parameters together with the calculated block volumes and neutron SLDs (**Table S1**) were then used to calculate theoretical SANS patterns for $PLMA_{39}$-$PMMA_{55}$ and $PLMA_{39}$-d_8PMMA_{57} nanoparticles, as well as for the $PLMA_{39}$-$PMMA_{94}$ and $PLMA_{39}$-d_8PMMA_{96} nanoparticle binary mixtures (**Figures 3A and 3B**).

Table S2. Summary of the fitting results obtained for SAXS patterns of 1.0% w/w dispersions of $PLMA_{39}$-$PMMA_x$ and $PLMA_{39}$-d_8PMMA_x nanoparticles in *n*-dodecane (both as prepared at 20 °C and after annealing to 150 °C for 30 min followed by cooling to 20 °C). Satisfactory data fits could only be obtained by assuming that no solvent was present within the nanoparticle cores. Errors on the R_g values correspond to the uncertainty in fitting this parameter.

Copolymer ID	Concentration, % v/v	Core radius (R_{core}), nm	Radius of gyration of the corona block (R_g), nm
$PLMA_{39}$-$PMMA_{55}$ (as prepared)	0.46	5.4 ± 0.6	2.05 ± 0.04
$PLMA_{39}$-$PMMA_{55}$ (after heating to 150 °C for 30 min)	0.46	5.4 ± 0.6	2.02 ± 0.04
$PLMA_{39}$-d_8PMMA_{57} (as prepared)	0.59	5.6 ± 0.5	1.99 ± 0.04
$PLMA_{39}$-d_8PMMA_{57} (after heating to 150 °C for 30 min)	0.53	5.5 ± 0.6	2.01 ± 0.04
$PLMA_{39}$-$PMMA_{94}$ (as prepared)	0.49	7.3 ± 0.7	2.00 ± 0.04
$PLMA_{39}$-$PMMA_{94}$ (after heating to 150 °C for 30 min)	0.47	7.3 ± 0.7	1.99 ± 0.04
$PLMA_{39}$-d_8PMMA_{96} (as prepared)	0.54	7.0 ± 0.6	2.00 ± 0.04
$PLMA_{39}$-d_8PMMA_{96} (after heating to 150 °C for 30 min)	0.55	7.2 ± 0.6	1.98 ± 0.04

Table S3. A summary of nanoparticle core and overall diameters and their standard deviations (in brackets) for PLMA$_{39}$-PMMA$_x$ and PLMA$_{39}$-d$_8$PMMA$_x$ spheres determined by SAXS analysis before and after thermal annealing at 150 °C for 30 min. The overall particle diameters were calculated by combining the core radius (R_{core}) with the R_g obtained for the PLMA$_{39}$ coronal chains (**Figure 2**) using the equation $D = 2R_{core} + 4R_g$.

Copolymer composition	Core diameter before annealing / nm	Core diameter after annealing / nm	Overall diameter before annealing / nm	Overall diameter after annealing / nm
PLMA$_{39}$-PMMA$_{55}$	10.8 (± 1.1)	10.8 (± 1.2)	18.9 (± 1.1)	18.9 (± 1.2)
PLMA$_{39}$-d$_8$PMMA$_{57}$	11.0 (± 1.0)	10.9 (± 1.1)	19.0 (± 1.0)	19.0 (± 1.1)
PLMA$_{39}$-PMMA$_{94}$	14.5 (± 1.4)	14.7 (± 1.3)	22.5 (± 1.4)	22.6 (± 1.3)
PLMA$_{39}$-d$_8$PMMA$_{96}$	13.9 (± 1.2)	14.4 (± 1.2)	21.9 (± 1.2)	22.4 (± 1.2)

SANS sample preparation details

Prior to TR-SANS measurements, equal volumes of 20% w/w hydrogenous and core-deuterated nanoparticle dispersions were mixed and subsequently diluted to 1.0% w/w solids using a judicious mixture of *n*-dodecane (38% v/v) and d$_{26}$-dodecane (62% v/v) (**Table S3**), such that the neutron SLD of this binary solvent mixture lies halfway between that of PMMA and d$_8$PMMA. If exchange of diblock copolymer chains between nanoparticles occurs on annealing such a binary mixture of dispersions, entropic mixing ensures that hybrid nanoparticle cores are obtained that comprise both hydrogenous and deuterated PMMA blocks. As a result, the core scattering length density should gradually become equal to that of the binary solvent mixture, which means that the neutron scattering intensity should be gradually reduced to a minimum value once copolymer chain exchange is complete.

The scattering length densities for the PMMA and d$_8$PMMA blocks, and the corresponding desired composition of the *n*-dodecane/d$_{26}$-dodecane binary solvent mixture, were calculated using **Equation S16**. Assuming ideal entropic mixing, the scattering length density of mixtures can be calculated as:

$$P_{total} = \sum \emptyset_i \times \xi_i \quad (S17)$$

where φ_i is the volume fraction of each component in the mixture, ξ_i is its scattering length density and summation is performed over the number of components in the mixture. A 1:1 mixed dispersion

by volume was prepared by combining 0.30 ml of a 20% w/w dispersion of PLMA$_{39}$-PMMA$_x$ nanoparticles in *n*-dodecane with 0.30 ml of a 20% w/w dispersion of PLMA$_{39}$-d$_8$PMMA$_x$ nanoparticles in the same solvent. The mean SLD of the mixed nanoparticle core was calculated to be 3.55 × 10^{10} cm^{-2}. Based on this value, this mixed dispersion was diluted to 1.0% w/w using a binary mixture of *n*-dodecane and d$_{26}$-dodecane so as to afford a final 38:62 v/v *n*-dodecane/d$_{26}$-dodecane solvent composition. This binary solvent was chosen because its neutron SLD lies halfway between that of the hydrogenous and deuterated PMMA cores (**Table S1**).

Table S4. Summary of the component volumes used to prepare the mixtures of hydrogenous and semi-deuterated nanoparticle dispersions used in the TR-SANS experiments. Judicious mixtures of 20% w/w dispersions of fully hydrogenous and core-deuterated PLMA$_{39}$-PMMA$_x$ (where x is either 55 or 94 for the hydrogenous species and x is either 57 or 96 for the core-deuterated species) nanoparticles were combined in a 1:1 ratio by volume and thereafter diluted to 1.0% w/w using the stated volumes of *n*-dodecane and d$_{26}$-dodecane. The same binary solvent mixture was made up for use as a background.

Composition	Volume of binary dispersion at 20% w/w / μl	Volume of *n*-dodecane / μl	Volume of d$_{26}$-dodecane / μl
Background solvent	-	229	371
PLMA$_{39}$-PMMA$_{55}$ + PLMA$_{39}$-d$_8$PMMA$_{57}$ 1:1 v/v ratio	47	186	367
PLMA$_{39}$-PMMA$_{94}$ + PLMA$_{39}$-d$_8$PMMA$_{96}$ 1:1 v/v ratio	47	186	367

3. Variable temperature proton NMR spectroscopy studies

(A) PLMA$_{39}$-PMMA$_{55}$ spheres in *n*-dodecane

(B) PLMA$_{39}$-PMMA$_{94}$ spheres in *n*-dodecane
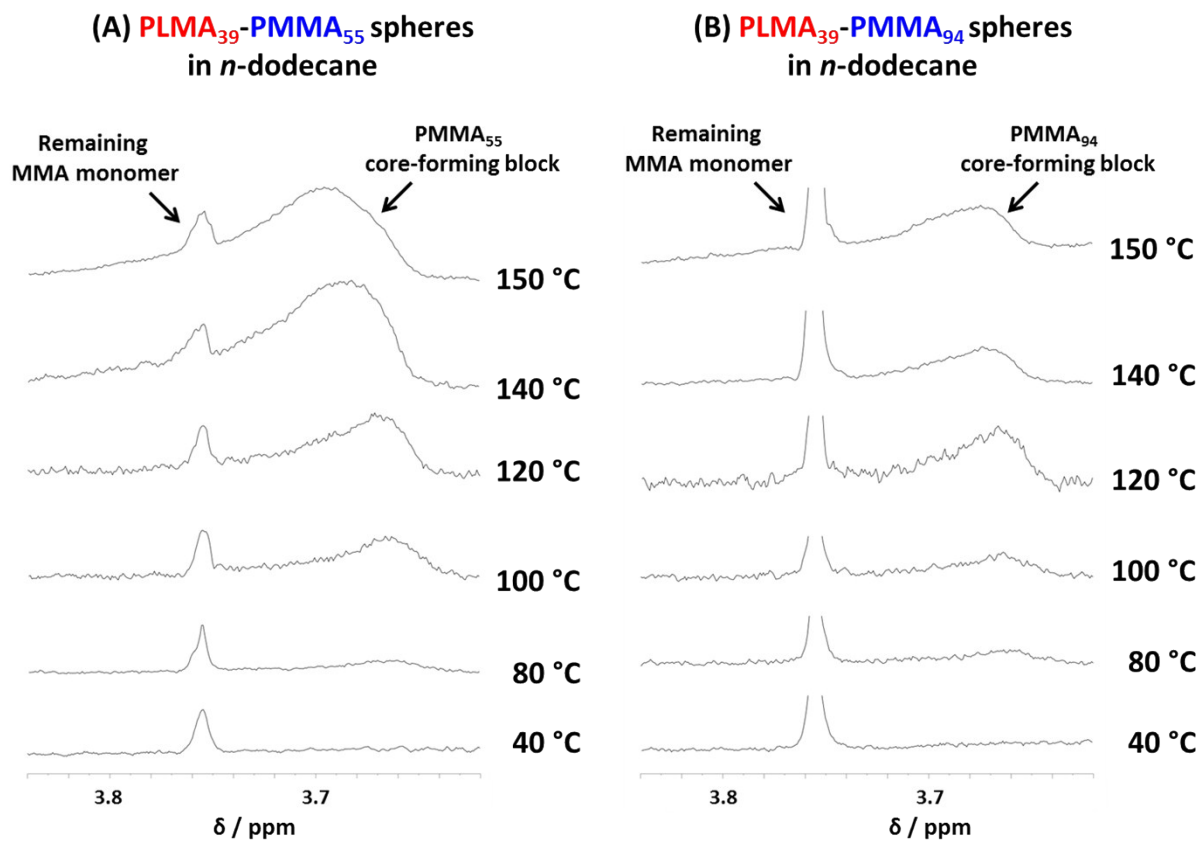
Figure S4. Variable temperature proton NMR spectra recorded from 40 °C to 150 °C for (a) PLMA$_{39}$-PMMA$_{55}$ and (b) PLMA$_{39}$-PMMA$_{94}$ spherical nanoparticles at 1.0% w/w in *n*-dodecane using an internal capillary tube containing d$_8$-DMSO as the lock solvent.

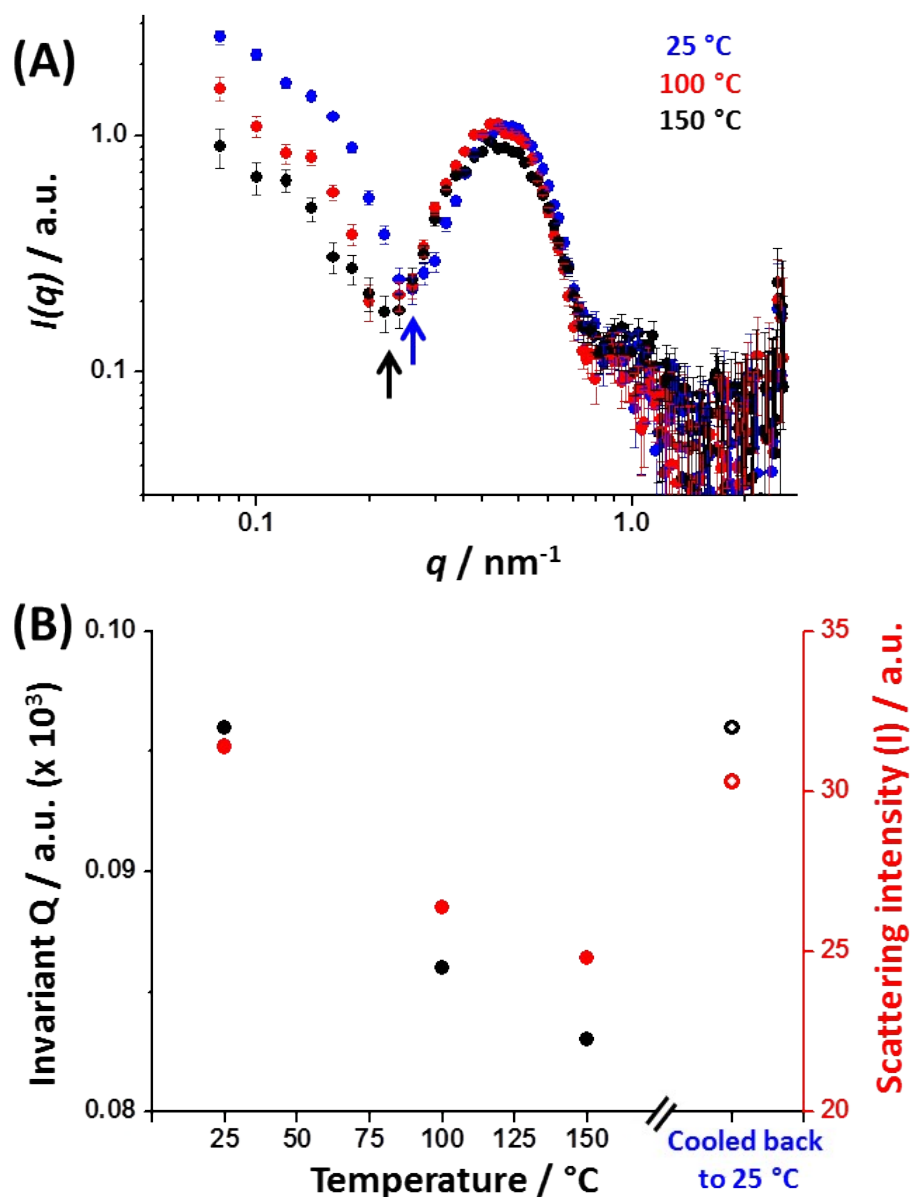## 4. Variable temperature SANS studies (Fig. S5) and $R(t)$ analysis (Fig. S6)

Figure S5. (A) Variable temperature SANS studies of PLMA$_{39}$-d$_8$PMMA$_{57}$ spheres in a binary solvent mixture consisting of 38% hydrogenous n-dodecane and 62% d$_{26}$-dodecane. The blue and black arrows in the $I(q)$ vs. q plot indicate the minima in the scattering patterns recorded at 25 °C and 150 °C, respectively. At higher temperature, these minima shift to lower q and the scattering intensity in this regime is reduced. Cooling this nanoparticle dispersion to 25 °C yields an identical SANS pattern to that originally recorded at this temperature. (B) Temperature dependence of the scattering invariant (Q) and total scattering intensity (I) for the same nanoparticles. Q and I are both reduced on heating and return to their (approximate) original values on cooling to 25 °C. This behavior is the result of partial solvation of the nanoparticle cores (and also expulsion of some diblock copolymer chains) at elevated temperature, which reduces the scattering contrast between the nanoparticle cores and the binary solvent mixture.

The equation used to calculate $R(t)$ is given below:

$$R(t) = \left(\frac{I_t - I_\infty}{I_0 - I_\infty}\right)^{1/2} \quad (S18)$$

Here I_0 represents the integrated scattering intensity at the beginning of the experiment at 40 °C, I_t is the integrated scattering intensity after an elapsed time (t) at each temperature, and I_∞ is the final integrated scattering intensity obtained at 150 °C.
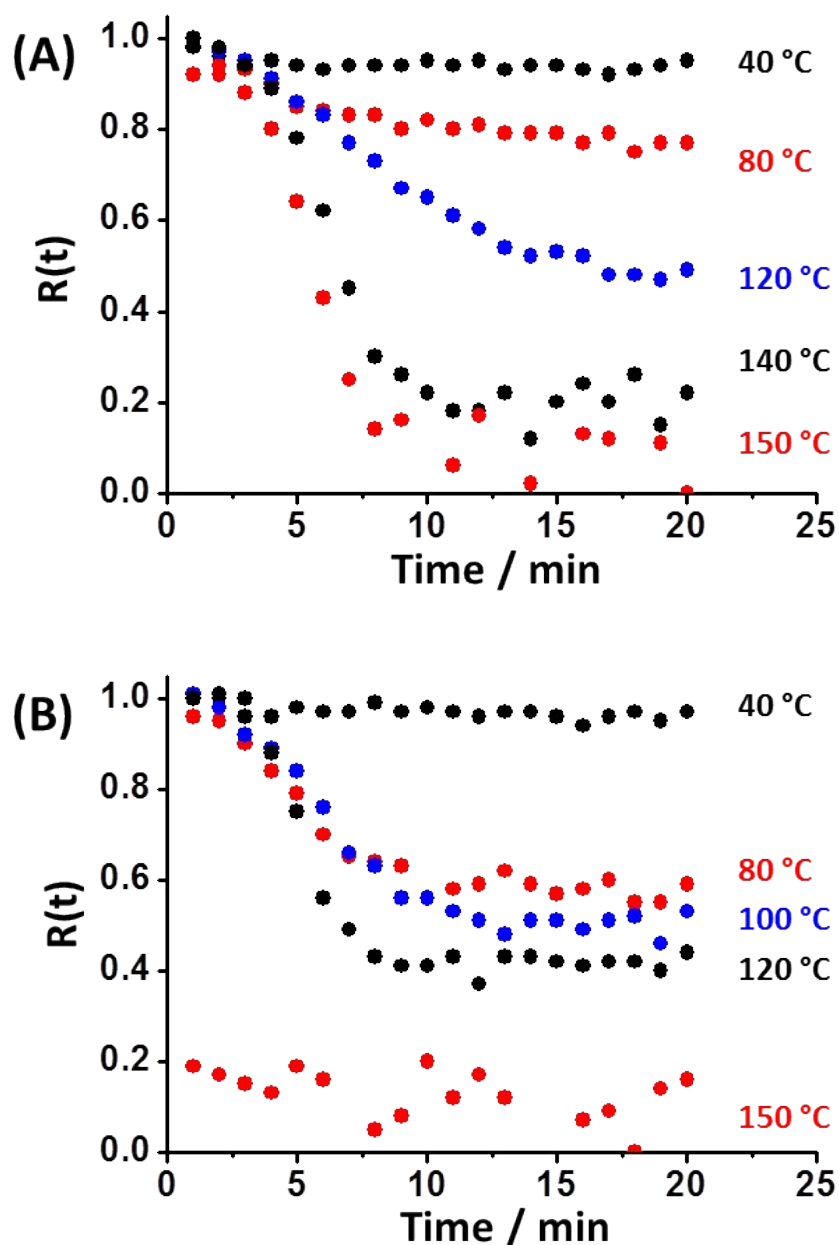

Figure S6. Heating binary mixtures of (A) PLMA$_{39}$-PMMA$_{94}$ and PLMA$_{39}$-d$_8$PMMA$_{96}$ nanoparticles of around 22 nm diameter and (B) PLMA$_{39}$-PMMA$_{55}$ and PLMA$_{39}$-d$_8$PMMA$_{57}$ nanoparticles of around 19 nm diameter causes a gradual reduction in $R(t)$ during TR-SANS experiments. This is the result of a progressive reduction in neutron contrast for the nanoparticle cores owing to copolymer chain exchange. As expected, higher temperatures result in faster rates of chain exchange between nanoparticles. $R(t)$ was calculated using **Equation S18.**

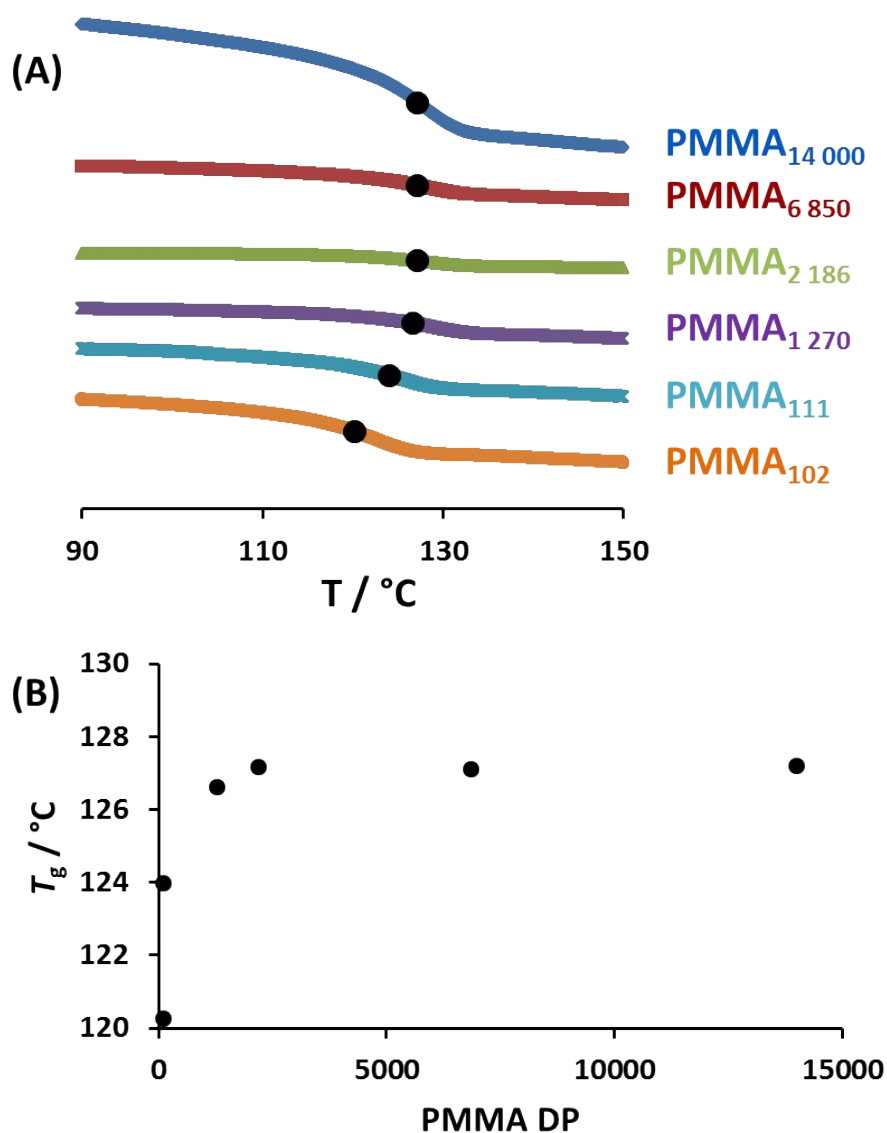## 5. DSC analysis of a series of PMMA homopolymers

Figure S7. (A) Differential scanning calorimetry curves obtained for a series of near-monodisperse PMMA homopolymers with mean degrees of polymerization (DP) ranging between 102 and 14 000 (black dots indicate the calculated glass transition temperature, T_g, in each case). (B) Plot of T_g against mean DP for the same series of PMMA homopolymers. In accordance with the Fox equation, lower DPs lead to lower T_g values; for example, PMMA$_{14\,000}$ has a T_g of 127 °C, whereas PMMA$_{102}$ has a T_g of 120 °C.

6. References

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