How Do Spherical Diblock Copolymer Nanoparticles Grow During RAFT Alcoholic Dispersion Polymerization?

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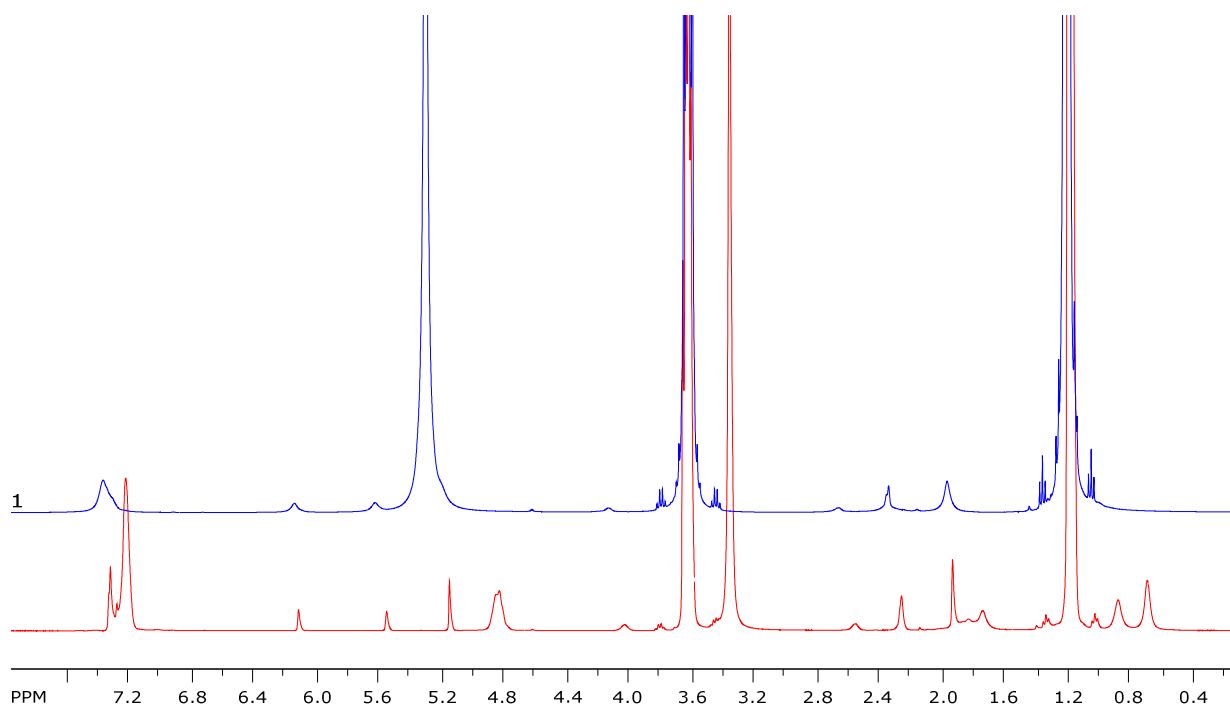
Figure S1. ^{1}H NMR spectra of $PDMA_{94}$-$PBzMA_{810}$ recorded in C_2D_5OD (upper spectrum) or CD_2Cl_2 (lower spectrum). The former spectrum gives an apparent composition of $PDMA_{94}$-$PBzMA_{64}$ because the core-forming PBzMA block is only *partially* solvated in ethanol. In contrast, CD_2Cl_2 is a good solvent for both blocks, so the PBzMA peaks are *fully* solvated in this solvent and the actual block composition can be calculated. In both cases, signals arising from residual BzMA monomer are observed at 5.6 and 6.1 ppm, which is expected given the incomplete conversion (81 %) for this synthesis. This unreacted BzMA monomer partially solvates the PBzMA core-forming chains in addition to the C_2D_5OD. However, the apparent block composition calculated above suggests that the degree of solvation is no more than 8 %, even in this case. Such ^{1}H NMR analyses were performed for all diblock copolymer nanoparticles described in this paper, with estimated degrees of solvation ranging from 5-13 %.

Spherical micelle model used for SAXS analysis

In general, the scattering intensity of a system comprising just one type of non-interacting polydisperse objects can be expressed as

$$I(q) = N \int_0^\infty ... \int_0^\infty F(q,r_1,...,r_k)^2 \Psi(r_1,...,r_k) dr_1...dr_k \qquad \text{(S1)}$$

where $F(q,r_1,...,r_k)$ is the form factor for the scattering objects, $\Psi(r_1,...,r_k)$ is the distribution function, N is the number density per unit volume of the objects and $r_1,...,r_k$ is a set of k parameters describing their structural morphology. The PDMA$_{94}$-PBzMA$_x$ diblock copolymer chains studied in this work self-assemble in ethanol to form spherical nanoparticles (or micelles) (Figure 2). Thus, the form factor in eq S1 can be expressed via an analytical expression previously reported for spherical copolymer micelles.[1]

$$F(q) = [N\beta_{mc}A_{mc}(q)]^2 + N_{agg}\beta_c^2 F_c(qR_g) + N_{agg}(N_{agg}-1)\beta_c^2 A_c^2(q) + 2N_{agg}^2\beta_{mc}\beta_c A_{mc}(q)A_c(q) \qquad \text{(S2)}$$

Here the X-ray scattering length contrast for the core block and the corona block is given by $\beta_{mc} = V_{mc}(\xi_{mc} - \xi_{sol})$ and $\beta_c = V_c(\xi_c - \xi_{sol})$, where ξ_{mc}, ξ_c, and ξ_{sol} are the X-ray scattering lengths of the core block (ξ_{PBzMA} = 10.67 $\times$ 10^{-10} cm^{-2}), the corona block (ξ_{PDMA} = 10.12 $\times$ 10^{-10} cm^{-2}) and the solvent ($\xi_{ethanol}$ = 7.57 $\times$ 10^{-10} cm^{-2}), respectively. V_{mc} and V_c denote the volumes of the core block (V_{PBzMAx}, see Table 2) and the corona block (V_{PDMA94} = 22.5 nm^3), respectively. These volumes were obtained from

$$V = \frac{M_w}{N_A \rho}$$ using the molecular weight (M_w) of the corresponding block and the solid-state homopolymer densities determined by helium pycnometry (ρ_{PBzMA} = 1.18 g cm^{-3} and ρ_{PDMA} = 1.09 g cm^{-3}). The spherical form factor amplitude is used for the amplitude of the micelle core self-term

$$A_{mc}(q) = \frac{3[\sin(qR_s) - qR_s\cos(qR_s)]}{(qR_s)^3} \qquad \text{(S3)}$$

where R_s is the radius of the spherical micelle core. The mean aggregation number for the spherical micelles is given by $N_{agg} = (1 - x_{sol})\frac{4\pi R_s^3}{3V_{mc}}$, where x_{sol} is the solvent fraction in the micelle core. The self-correlation term of the corona block is described by the Debye function:

$$F_c(qR_g) = \frac{2[\exp(-q^2R_g^2) - 1 + q^2R_g^2]}{q^4 R_g^4} \qquad \text{(S4)}$$

where R_g is the radius of gyration of the corona block. For diblock copolymers with a relatively short PBzMA block DP, the corona contribution to the scattering is comparable to the scattering from the micelle core [i.e. PDMA$_{94}$-PBzMA$_{100}$ with $(\beta_c / \beta_{mc})^2 \approx 0.26$]. Thus, in accordance with previous work,[2] the amplitude of the corona self-term was obtained from a normalized Fourier transform of the radial density distribution function of the PDMA$_{94}$ coronal chains in the micelle.

$$A_c(q) = \frac{\int\limits_{R_s}^{R_s+2s} \mu_c(r)\dfrac{\sin(qr)}{qr}r^2 dr}{\int\limits_{R_s}^{R_s+2s} \mu_c(r)r^2 dr} \tag{S5}$$

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 profile and the weight coefficient, respectively.[3] The precise analytical expression of the integration applied in the SAXS analysis is not given in the reference but it can be obtained by using a mathematical software package such as Maple or MatLab. An approximate integration can also be found elsewhere.[4] In accordance with previous studies[2-4] a confinement $s = 2R_g$ was introduced into the model. It is known that a tends to zero for this condition, so it was assumed that $a = 0$. For the form factor given by eq S2, no penetration of the corona blocks into the micelle cores and a sharp, non-sigmoidal interface between the blocks was assumed. A polydispersity for the spherical micelle core radius (R_s), expressed as a Gaussian distribution, is considered for the spherical micelles in eq S1:

$$\Psi(r_1) = \frac{1}{\sqrt{2\pi\sigma_{Rs}^2}}\, e^{-\frac{(r_1-R_s)^2}{2\sigma_{Rs}^2}} \tag{S6}$$

where σ_{Rs} is the standard deviation for R_s. The number density per unit volume in eq S1 is expressed as:

$$N = \frac{c}{\int\limits_{0}^{\infty} V(r_1)\Psi(r_1)dr_1} \tag{S7}$$

where c is the total copolymer volume fraction in the spherical micelles and $V(r_1)$ is the total copolymer volume in a spherical micelle [$V(r_1) = (V_{mc} + V_c)N_{agg}(r_1)$]. Thus, the overall number of structural parameters for the spherical micelle model described by eq S1 and eq S2 is seven (R_s, σ_{Rs}, x_{sol}, R_g, s, a and c). Four of these seven parameters are determined independently, leaving just three variable parameters available for modelling.

Differential refractive index measurements

Differential refractive index (dn/dc) values were obtained for each of the PDMA$_{94}$-PBzMA$_x$ diblock copolymer spherical nanoparticles using a Wyatt Optilab T-rEX differential refractometer. Nanoparticle dispersions were prepared in ethanol at copolymer concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mg mL^{-1} and then injected consecutively into the instrument (lowest concentration first). Figure S1 illustrates a typical data set obtained for PDMA$_{94}$-PBzMA$_{392}$ nanoparticles. Plotting a calibration graph of dRI against copolymer concentration allows the dn/dc to be calculated directly from the linear gradient (see inset in Figure S1).
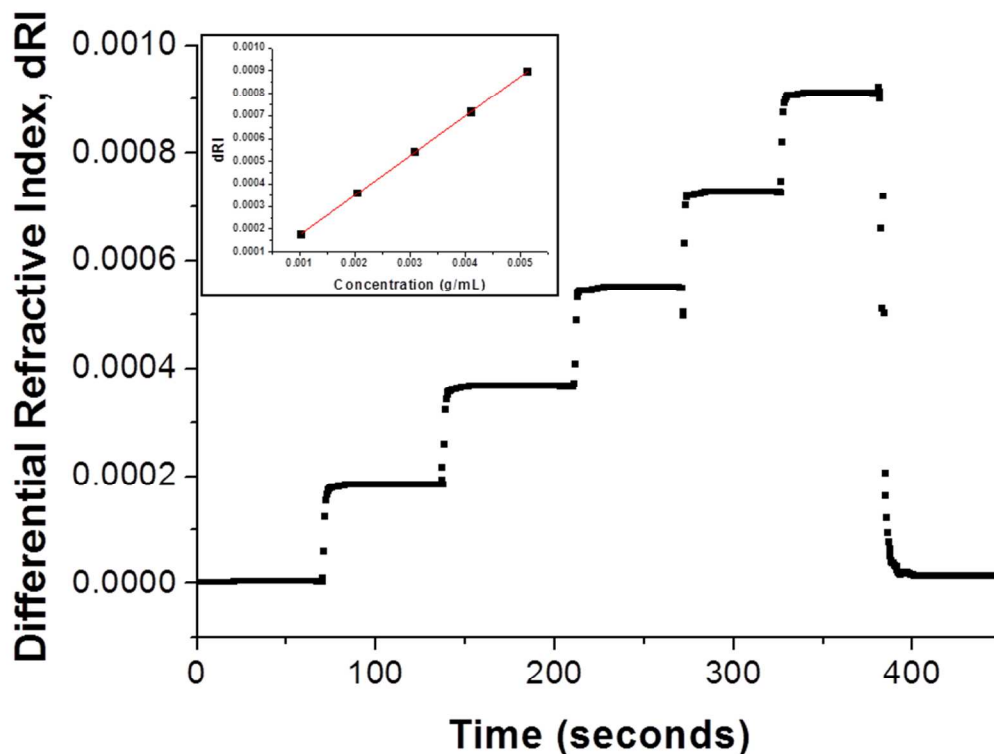
Figure S2. Change in refractive index, dRI, for a series of five PDMA$_{94}$-PBzMA$_{392}$ nanoparticle concentrations determined using a Wyatt Optilab T-rEX instrument equipped with Astra software. Inset is the plot of dRI against copolymer concentration, which was subsequently used to calculate the differential refractive index (dn/dc) for these nanoparticles.
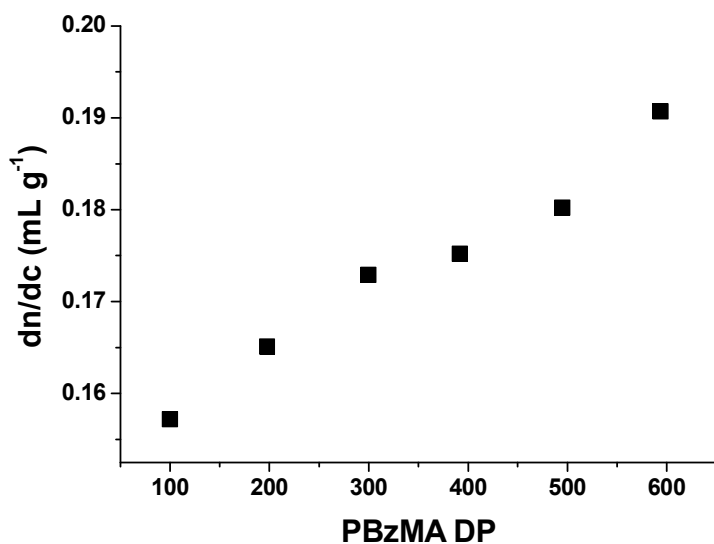

Figure S3. Summary of dn/dc values calculated for a series of PDMA$_{94}$-PBzMA$_x$ diblock copolymer nanoparticles using a Wyatt Optilab T-rEX differential refractometer and Astra software (provided by the manufacturer).

Molecular weight determination from MALLS data

Debye formalism: $\dfrac{R_\theta}{Kc} = MP(\theta) - 2A_2cM^2P^2(\theta)$

Zimm formalism (reciprocal method): $\dfrac{Kc}{R_\theta} = \dfrac{1}{MP(\theta)} + 2A_2c$

Berry formalism (square root method): $\sqrt{\dfrac{Kc}{R_\theta}} = \dfrac{1}{\sqrt{MP(\theta)}} + A_2c\sqrt{MP(\theta)}$

For spheres: $P(\theta) = \left(\left(\dfrac{3}{x^3}\right)(sinx - xcosx)\right)^2$

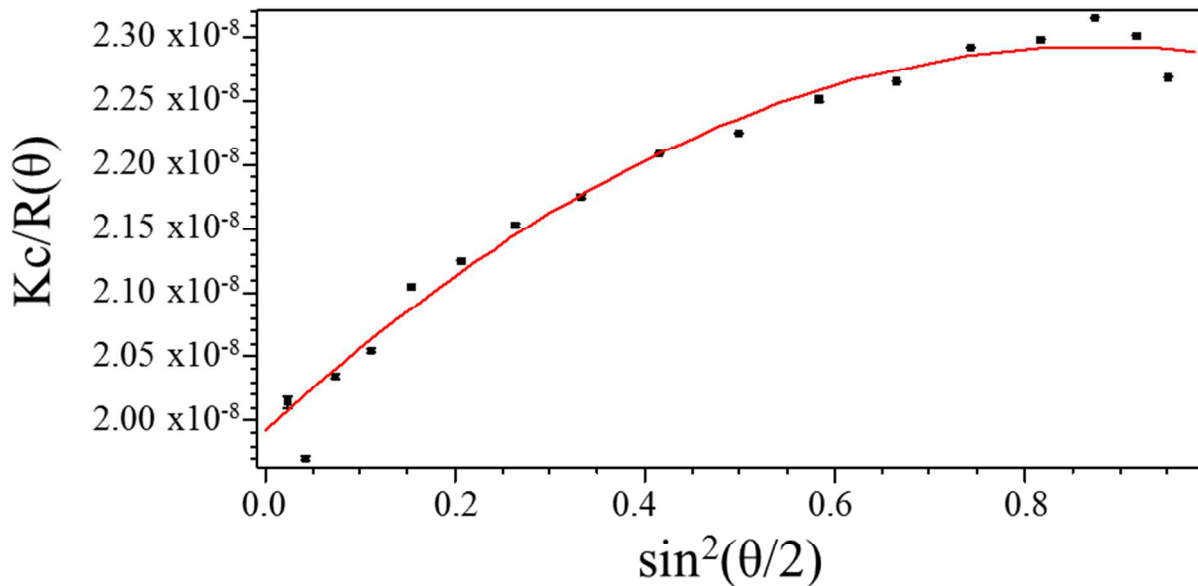Where: $x = 2\pi\left(\dfrac{D}{\lambda}\right)sin\left(\dfrac{\theta}{2}\right)$ (D = sphere diameter)

Figure S4. Representative MALLS plot using the Zimm formalism for light scattering data obtained for PDMA$_{94}$-PBzMA$_{392}$ diblock copolymer micelles dispersed in ethanol. The weight-average molecular weight (M_w) of these micelles was determined to be 5.001 x 10^7 g mol^{-1}, which indicates a micelle aggregation number, N_{agg}, of 443.
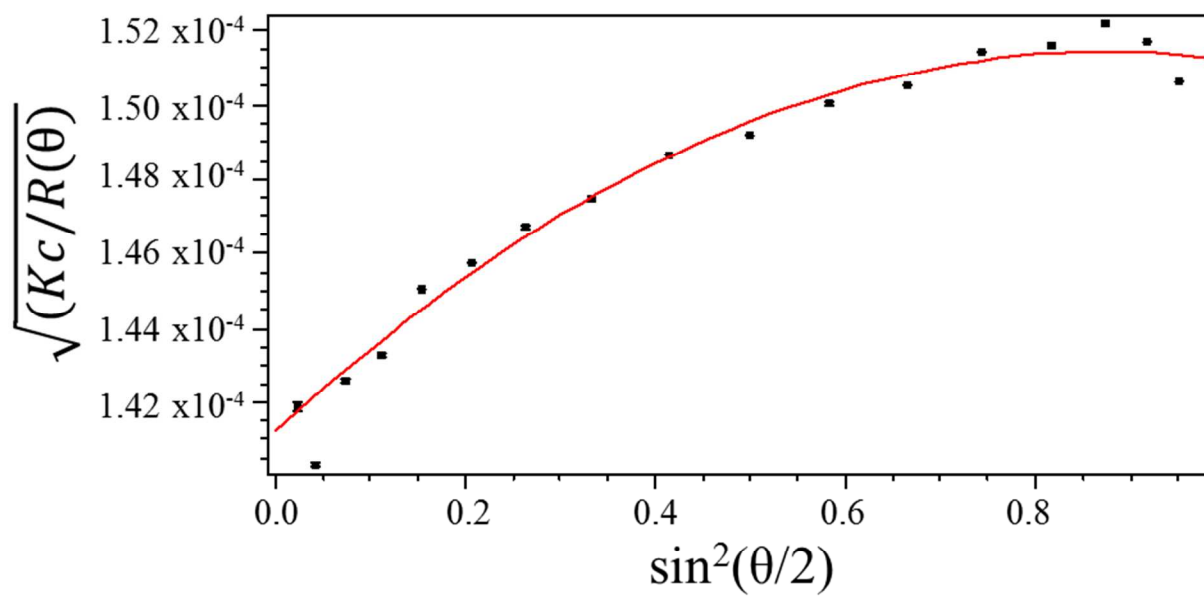
Figure S5. Representative MALLS plot obtained using the Berry formalism to analyse light scattering data obtained for PDMA$_{94}$-PBzMA$_{392}$ diblock copolymer nanoparticles dispersed in ethanol. The weight-average molecular weight (M_w) for these micelles was determined to be 5.01 x 10^7 g mol^{-1}, which indicates a mean micelle aggregation number, N_{agg}, of 444.

Table S1. Weight-average molecular weights determined by MALLS for PDMA$_{94}$-PBzMA$_x$ diblock copolymer nanoparticles using the three most commonly used analytical methods, and the corresponding mean micelle aggregation numbers.

Composition	Analysis Method	M$_W$	N$_{agg}$
PDMA$_{94}$-PBzMA$_{100}$	Zimm	5.83 x 10^6	133
	Debye	5.81 x 10^6	132
	Berry	5.82 x 10^6	133
PDMA$_{94}$-PBzMA$_{198}$	Zimm	1.77 x 10^7	268
	Debye	1.76 x 10^7	266
	Berry	1.77 x 10^7	268
PDMA$_{94}$-PBzMA$_{392}$	Zimm	5.01 x 10^7	444
	Debye	4.98 x 10^7	441
	Berry	5.00 x 10^7	443
PDMA$_{94}$-PBzMA$_{495}$	Zimm	7.35 x 10^7	532
	Debye	7.30 x 10^7	528
	Berry	7.37 x 10^7	533
PDMA$_{94}$-PBzMA$_{594}$	Zimm	1.01 x 10^8	685
	Debye	9.90 x 10^7	672
	Berry	9.96 x 10^7	676

Figure S6. MALLS plots obtained using the Debye formalism for each of the $PDMA_{94}$-$PBzMA_x$ diblock copolymer nanoparticles dispersed in ethanol. The associated weight-average molecular weights (M_w) and calculated mean aggregation numbers, N_{agg}, are listed in Table S1.
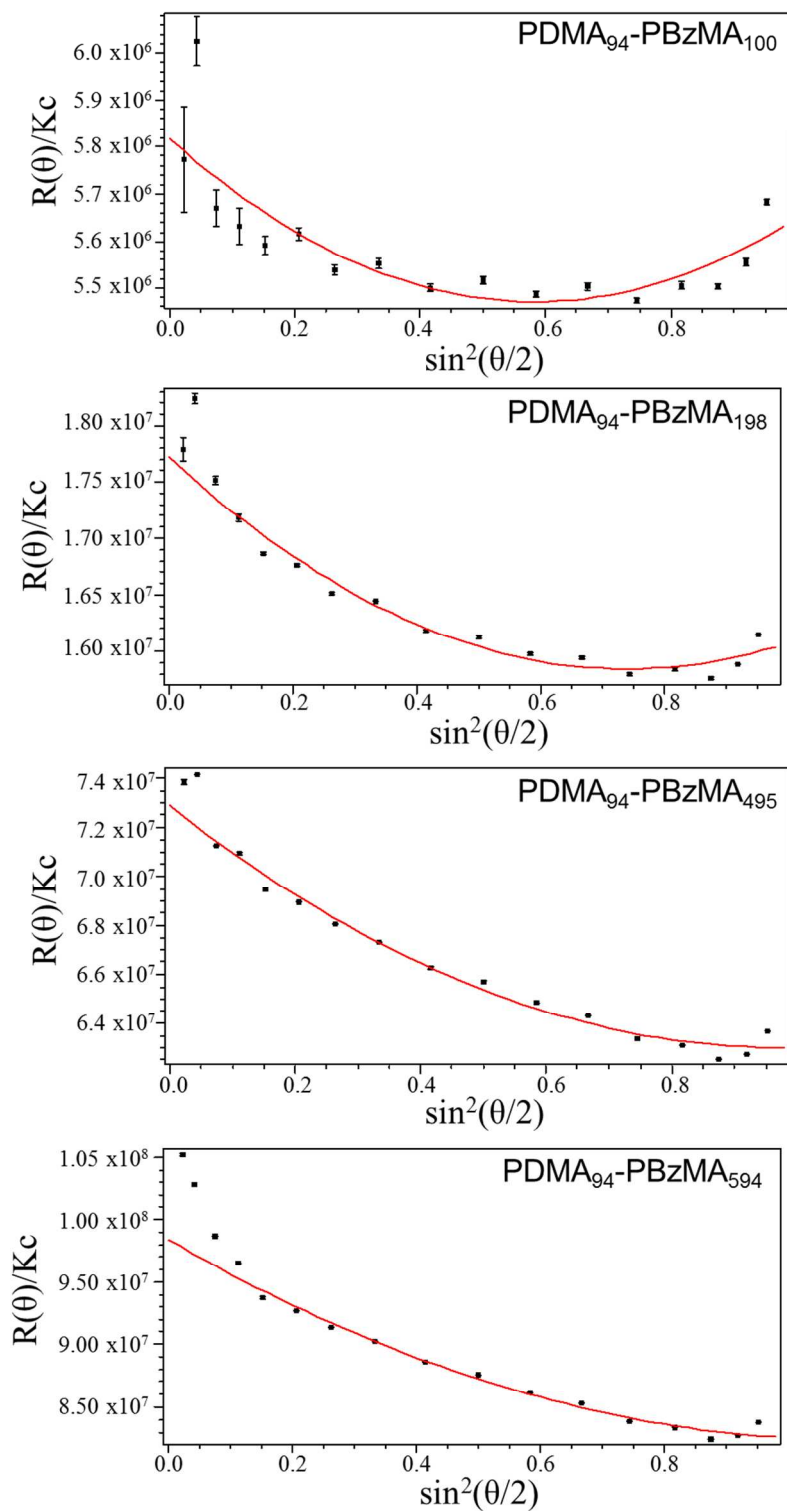
References

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