Thermoreversible gels composed of colloidal silica rods with short-range attractions

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SUPPORTING INFORMATION

The following equations for the form factor of polydisperse cylinders is restated for convenience from the NIST Center for Neutron Research Igor software package,[1] SasView software package,[2] which are based on other references.[3]

The averaged form factor P(q) for a system containing polydisperse cylinders of length L and radius R is given as:

$$P(q) = \frac{Scale}{V_{avg}} \int_0^x \int_0^y f(R) f(L)\, dR dL \int_0^{\pi/2} F^2(q,\alpha) \sin\alpha \, d\alpha + B \qquad (S1)$$

$$F(q,\alpha) = 2(\rho_{cyl} - \rho_{sol}) V_{cyl} \frac{\sin\left(q\, {}^{L}\!/_{2} \cos\alpha\right)}{q\, {}^{L}\!/_{2} \cos\alpha} \frac{J_1(qR \sin\alpha)}{qR\sin\alpha} \qquad (S2)$$

with the Schulz distribution of an arbitrary variable x:

$$f(x) = \frac{1}{Norm}(z+1)^{z+1} \left(\frac{x}{x_{avg}}\right)^z \frac{\exp\left(-\frac{x}{x_{avg}}(z+1)\right)}{x_{avg}\Gamma(z+1)} \qquad (S3)$$

$$z = \frac{1-p^2}{p^2} \qquad (S4)$$

The variables include the scattering vector (q), a scaling factor (Scale or volume fraction), the averaged cylinder volume (V_{avg}), the Schulz distributions for the cylinder length f(L) and radius f(R) described by Eq. S3 and Eq. S4, the angle between the cylinder length axis and q-vector (α), the incoherent background scattering (B), the scattering length density of the cylinder (ρ_{cyl}) and the solvent (ρ_{sol}), the cylinder volume of length L and radius R (V_{cyl}), the first order Bessel function (J_1), a normalization factor for the Schulz distribution (Norm), the gamma function Γ(z+1), and the polydispersity parameter in length (PD = p = σ_L/L_{mean}) and radius (σ_R/R_{mean}) based on the standard deviation σ and mean length or radius.

As shown in Eq. (S1), the cylinder form factor is averaged over all possible cylinder orientations, and it is averaged over the normalized Schulz distributions of length and radius. Eq. S1 is fit to experimental data as implemented in SasView software package v3.1.2. Additional smearing of the form factor due to instrument resolution and slit smearing is also implemented in SasView. At the examined low particle volume fractions, the structure factor S(q) = 1 for all q, which was confirmed by varying the rod concentration in the dilute regime ($\phi < 0.002$). Note that the polydispersity in length weakly influences the resulting form factor, with only slight influence occurring near $q \sim 2\pi/L_{avg}$. The dominant fitting parameters (excluding the scattering length density difference, the scale parameter, and the incoherent background) include the average radius R, average length L, and polydispersity in R.

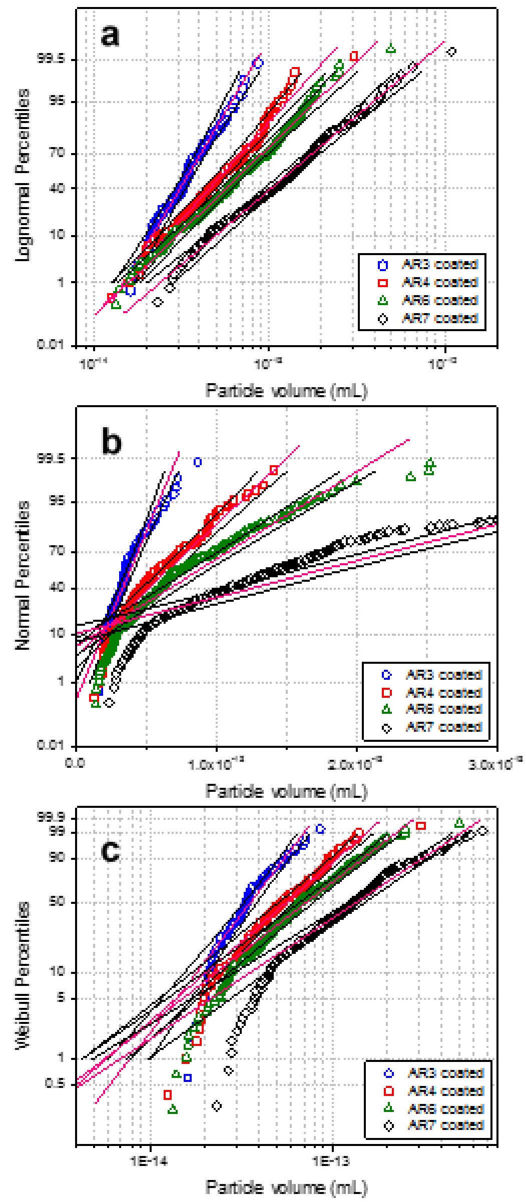

Figure S1. Probability plots for (a) Log-normal, (b) Normal, and (c) Weibull distributions of the coated silica rod particle volume. The particle volume was calculated from average dimensions determined from SEM, assuming a hemispherocylinder shape. Coated samples for AR3 (blue circles), AR4 (red squares), AR6 (green triangles), and AR7 (black diamonds) showed better agreement with the Log-normal distribution, which is shown by the linear reference line (solid pink lines) within the 95% confidence bands (solid black lines). The Normal or Weibull distributions showed stronger deviations from linearity.

Table S1. USAXS fitting parameters in the polydisperse cylinder form factor model.

Sample	AR3 calcined	AR4 calcined	AR6 calcined	AR7 calcined
Background, B (cm^{-1})	0.11	0.13	0.13	0.13
Average Length, L_{mean} (Å)	8413	12009	16839	20317
Average Radius, R_{mean} (Å)	1322	1304	1258	1497
Scale (volume fraction)	1.78E-03	1.74E-3	1.83E-3	1.84E-3
SLD cylinder ($Å^{-2}$)	1.76E-05	1.76E-05	1.76E-05	1.76E-05
SLD solvent ($Å^{-2}$)	7.60E-06	7.60E-06	7.60E-06	7.60E-06
Length PD ($p = \sigma_L/L$)	0.15	0.28	0.16	0.36
Radius PD ($p = \sigma_R/R$)	0.22	0.21	0.27	0.26
χ^2/N	38.0	20.5	27.2	26.4

Table S1 shows the parameters used in the polydisperse cylinder form factor model fit to dilute calcined rods suspended in ethanol. Parameters included the incoherent background scattering, cylinder length, cylinder radius, scale (volume fraction), cylinder scattering length density (SLD), solvent SLD, length polydispersity ($p = \sigma_L/L_{mean}$) assuming a Schulz distribution, radius polydispersity, and the resulting normalized chi-squared error between the model fit and experimental data. The background, cylinder SLD, and solvent SLD were fixed parameters, whereas all other parameters were fit using the initial guesses determined from SEM size distributions. The size parameters determined from USAXS and the polydisperse cylinder model fit were in good agreement with SEM measurements (refer to Table 1 in main text).

Table S2. USAXS background and normalization constants for coated silica rods.

Sample	T (°C)	B (cm^{-1})	C
AR3 coated	40	0.10	0.26
AR4 coated	40	0.10	0.48
AR6 coated	40	0.10	0.23
AR7 coated	40	0.11	0.30
AR3 coated	20	0.10	0.59
AR4 coated	20	0.11	0.74
AR6 coated	20	0.11	0.66
AR7 coated	20	0.11	0.40

Table S2 shows the subtracted background constant (B) and the normalization constant (C) used in Fig. 5 (main text) to scale the high-q regime ($q > 0.005$ Å^{-2}) and to compare the scattering curves of coated silica rods suspended in tetradecane to the calcined silica rods suspended in ethanol.

References

1. Kline, S. R. Reduction and analysis of SANS and USANS data using IGOR Pro. *J Appl Crystallogr* **2006,** *39* (6), 895-900.
2. SasView. http://www.sasview.org/.
3. Guinier, A.; Fournet, G. *Small-Angle Scattering of X-rays*; John Wiley and Sons: New York, 1955.