Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information:

Controllable synthesis and self-assembly of $PbCO_3$ nanorods in shape-dependent nonionic w/o microemulsions

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S1. SAXS measurements on the microemulsions

In order to check whether the microemulsion structure changes by adding deuterated compounds and salts and during the reactions, small angle X-ray scattering (SAXS) investigations on the microemulsions were further performed with a home-built NanoStar instrument from Bruker AXS with a Microfocus X-ray source (IμS) operated at 50 kV and 600 μA. The emitted radiation is collimated by a pinhole geometry and monochromatized to the Cu K-α line of λ =1.54 Å. A VÅNTEC 2000 xenon gas filled detector with 2048×2048 pixels was used to record the 2D scattering patterns at a sample-to-detector distance of 105 cm, resulting in an accessible q-range of $0.06<q< 3$ nm^{-1}. The collected data were corrected for detector sensitivity, empty cell scattering, background noise and transmission, and calibrated to absolute units [cm^{-1}] using a secondary standard: FEP1400A from Dupont.

As shown in Fig. S1, the SAXS curves of $H_2O/C_{12}E_5$/hexane and $D_2O/C_{12}E_5$/*d*-hexane are almost overlapping on each other. It reveals that the use of the deuterated solvents and D_2O has little effect on the structure of the parental microemulsions for nanoparticle synthesis.

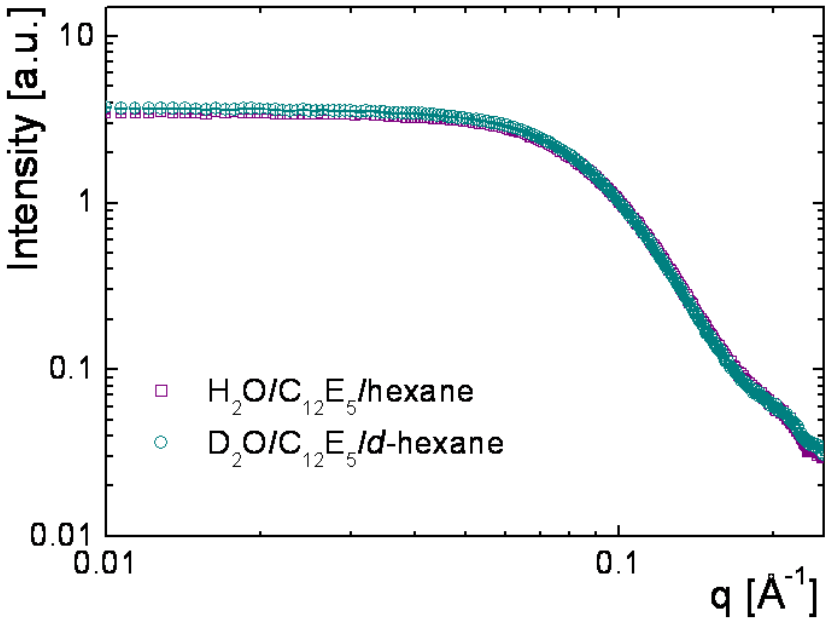

Fig. S1 SAXS data from $H_2O/C_{12}E_5$/hexane and $D_2O/C_{12}E_5$/*d*-hexane microemulsions, at w/s=0.2 (weight ratio), 13.6 wt % surfactant concentration, and room temperature.

As can be seen in Fig. S2, the incorporated salt solutions have little effect on the size and shape of the nonionic microemulsions that were used for the synthesis of the nanoparticles. This is because nonionic microemulsions are less sensitive to the addition of electrolytes, as compared to ionic surfactant-based microemulsions. Moreover, SANS measurements also verified that the structure of the microemulsions after the reaction is still kept the same as that before the reaction.

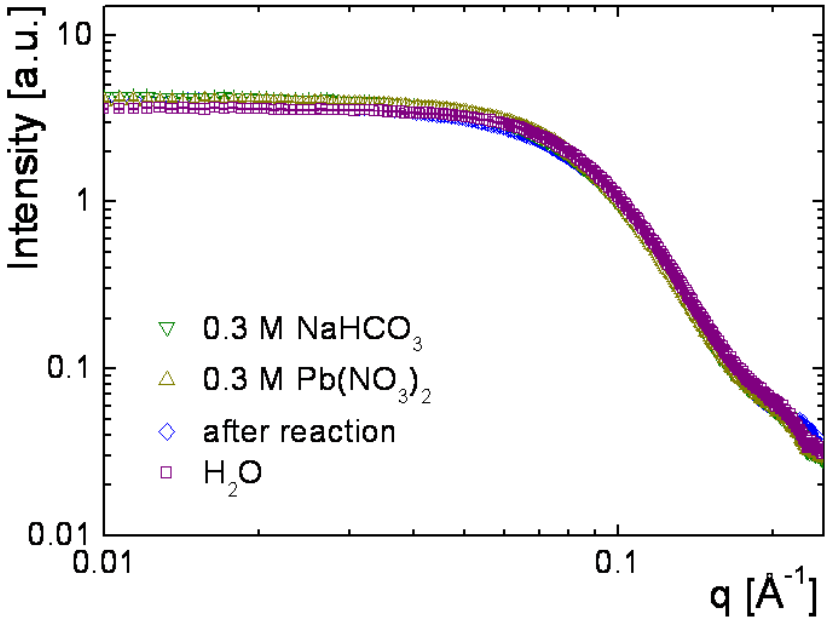

Fig. S2 SAXS data from $C_{12}E_5$/hexane reverse microemulsions using either H_2O or salt solutions as water phases, and the data measured after the reaction, at w/s=0.2 (weight ratio), 13.6 wt % surfactant concentration, and room temperature.

For Igepal system, SAXS has also been performed to check the structure of the microemulsion droplets before and after the reaction. It is shown in Fig. S3 that the size and shape of the cylindrical microemulsions does not change after the reaction, indicating that the water/surfactant ratio of the microemulsions has little change. Note that background scattering from capillary and solvents is strong and varies from each other at the low-*q* range.

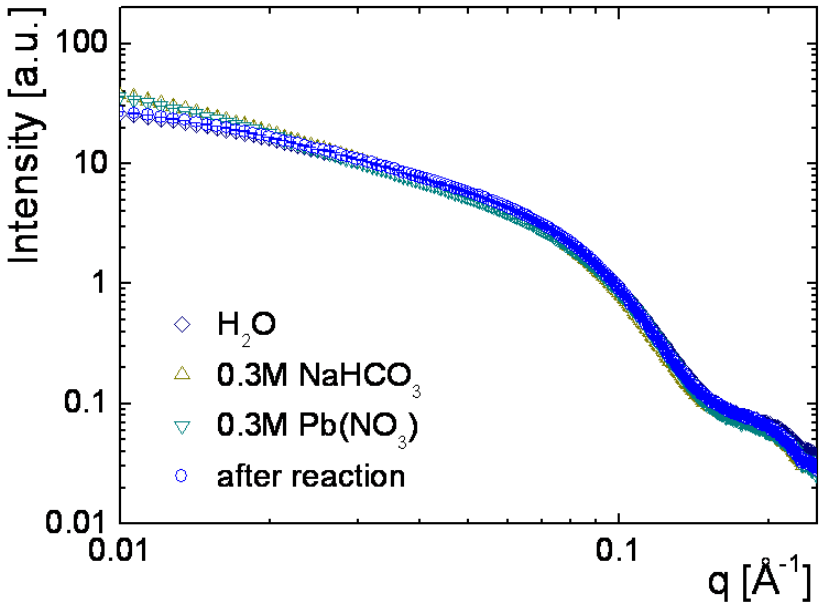

Fig. S3 SAXS data from Igepal/hexane reverse microemulsions using either H_2O or salt solutions as water phases, and the data measured after the reaction, at w/s=0.2 (weight ratio), 13.6 wt % surfactant concentration, and room temperature.

S2. SANS model fitting

All SANS fits shown in the maintext have been carried out using the DANSE fitting program, employing an iterative least-squares method.[1]

The SANS data of $C_{12}E_5$/hexane and Igepal/cyclohexane microemulsions are fitted using a core-shell hard sphere model. The form factor is given by [2]

$$P(q) = \frac{scale}{V_s}\int_0^{2\pi} F^2(q,r)g(r)dr \tag{1}$$

$$F(q,r) = 3V_c(\rho_c - \rho_s)\frac{\left[\sin(qr) - qr\cos(qr)\right]}{(qr)^3} + 3V_s(\rho_s - \rho_{solv})\frac{\left[\sin[q(r+t)] - q(r+t)\cos[q(r+t)]\right]}{[q(r+t)]^3} \tag{2}$$

where *scale* is a scale factor, V_s is the volume of the outer shell, V_c is the volume of the core, r is the radius of the core, t is the thickness of the shell, ρ_c is the scattering length density of the core, ρ_s is the scattering length density of the shell, ρ_{solv} is the scattering length density of the solvent. g(r) is the log-normal distribution function describing the polydispersity of homogeneous particles.

The interparticle structure factor for spherical particles through hard sphere (excluded volume) interactions is applied to get a better fit in a low-q range. The calculation uses the Percus-Yevick closure where the interparticle potential is [3]

$$U(r') = \begin{cases} \infty, r' < 2R \\ 0, r' \geq 2R \end{cases} \tag{3}$$

where r' is the distance from the center of the sphere with the effective radius R. In the fitting, the outer most radius (= $r + t$) is used as the effective radius toward S(Q). For an analytic expression of the Percus-Yevick hard sphere structure factor see e. g. ref 4.[4]

The SANS data of Igepal/hexane microemulsions and the mixture of $C_{12}E_5$/hexane and Igepal/hexane microemulsions are fitted using a core-shell cylinder model. The form factor for a circular cylinder with a core-shell scattering length density profile is given by [5]

$$P(q) = \frac{scale}{V_s} \int_0^{2\pi} F^2(q,\alpha)\sin(\alpha)d\alpha \tag{4}$$

$$\begin{aligned} F(q,r) = {} & 2(\rho_c - \rho_s)V_c \frac{\sin(\tfrac{1}{2}qL\cos\alpha)}{\tfrac{1}{2}qL\cos\alpha} \frac{J_1(qr\sin\alpha)}{qr\sin\alpha} \\ & + 2(\rho_s - \rho_{solv})V_s \frac{\sin\left[\tfrac{1}{2}q(L+t)\cos\alpha\right]}{\tfrac{1}{2}q(L+t)\cos\alpha} \frac{J_1[q(r+t)\sin\alpha]}{q(r+t)\sin\alpha} \end{aligned} \tag{5}$$

where α is the angle between the axis of the cylinder and the *q*-vector. The outer radius of the shell is given by (r+t) and the total length of the outer shell is given by (L+$2t$). J_1 is the first order Bessel function.

In the DANSE program, the fitting form factor parameters are core radius *r*, shell thickness *t*, cylinder length *L*, while the scattering length density is known. The experimental smearing of the SANS data due to the instrumental resolution, which leads to the smoothing in observing the minima of the oscillation from the form factor, was not taken into account. Instead, the smearing from the polydispersity is applied in the fitting as a compensation, by assuming a distribution only in the particle core size and cylinder length, while the shell thickness is fixed. From the fits, the polydispersity for the radius and cylinder length is around 30%, which is, as expected, higher than the normal value of the microemulsions (~10%).

S3. SANS data fitting using the ellipsoid model for all systems

To further check the rationality of the fit by the DANSE program, we performed non-linear least squares fittings to the SANS-data using the particle scattering factor, *P(q,A,ε)* of a core shell ellipsoid of revolution, [6-8] which is given by

$$P(q,A,\varepsilon) = \int_0^{\pi/2} \left[\frac{1}{M} \left(\Delta\sigma_s V\left(A,\varepsilon\right) F\left(q, R\left(A,\varepsilon,\alpha\right)\right) + \left(\Delta\sigma_c - \Delta\sigma_s\right) V_c\left(A_c,\varepsilon_c\right) F\left(q, R_c\left(A_c,\varepsilon_c,\alpha\right)\right)\right)\right]^2 \cos\alpha \, d\alpha$$

The parameters with the subscript *c* refer to properties of the core, those without a subscript refer to the outer dimensions of the ellipsoid, while those with subscript *s* refer to the shell only. The minor semiaxis is denoted as *A*, the corresponding ellipticities with ε and $\Delta\sigma$ is the scattering length density difference with respect to the suspending solvent. *F(q, R)* is the well known scattering amplitude of a homogeneous sphere with radius *R*, and M is defined as $M = \Delta\sigma_s V\left(A_s,\varepsilon_s\right) + \left(\Delta\sigma_c - \Delta\sigma_s\right) V_c\left(A_c,\varepsilon_c\right)$, where $V = 4\pi\varepsilon A^3/3$ is the volume of the respective spheroid

In the present case we applied shell contrast, therefore $\Delta\sigma_c$ was fixed to zero during the fitting, and the ellipticities of core and shell were forced to be equal. Therefore the model function has the five fitting parameter $A, A_c, \varepsilon, \Delta\sigma_s$ and *C*, which is the proportionality constant relating the scattered intensity to *P(q,A,ε)*

The experimental smearing of the SANS data due to wavelength spread, angular uncertainty and limited detector resolution, was taken into account by convoluting the model function with the instrument resolution function, as proposed by Pedersen. [9]

To minimize the effect of the structure factor, i. e. finite droplet concentration on the fitting parameters, we limited the *q*-range of the experimental data to values where the structure factor will not deviate significantly from unity. Explicitly, we used only scattering data at $q > 0.5\ \mathrm{nm}^{-1}$ since there the form factor of a hard sphere system will not deviate more than 10 % from unity at the given volume fraction.[10]

As shown in Fig. S4, the fits are quite well at $q > 0.5$ nm^{-1}. More importantly, the refined parameters agree well with the fits by DANSE program, except the elipticity for Igepal/cyclohexane system. The structure parameters are listed in Table S1.

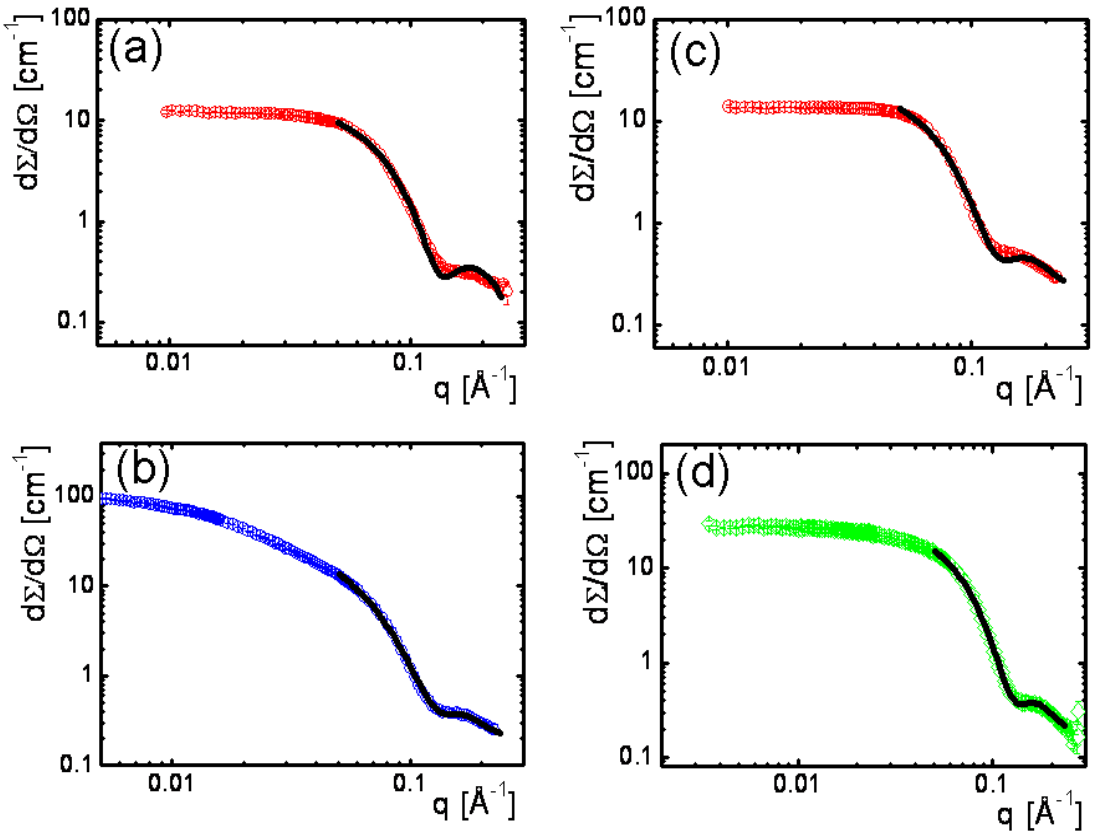

Fig. S4 SANS data of $C_{12}E_5$/hexane (a), Igepal/hexane (b), Igepal/cyclohexane (c), and 50% $C_{12}E_5$/hexane-50%Igepal/hexane (d) microemulsions. Solid curves represent the fits ($q > 0.5$ nm^{-1}) with a core-shell ellipsoid model by considering instrumental resolution smearing while neglecting the structure factor.

Table S1 The structure parameters of the microemulsions from the fit of the SANS curves by a core-shell ellipsoid model.

microemulsions	A (nm)	A_c (nm)	ε
$C_{12}E_5$/hexane	3.331	0.786	0.943
Igepal/hexane	3.131	0.871	8.754
Igepal/cyclohexane	3.073	0.711	1.485
50% $C_{12}E_5$/hexane-50% Igepal/hexane	3.181	0.958	1.496

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