Changes of microemulsion structure during polymerization of aqueous and organic phases – Supporting Information –

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SAXS curves of aqueous and organic phases

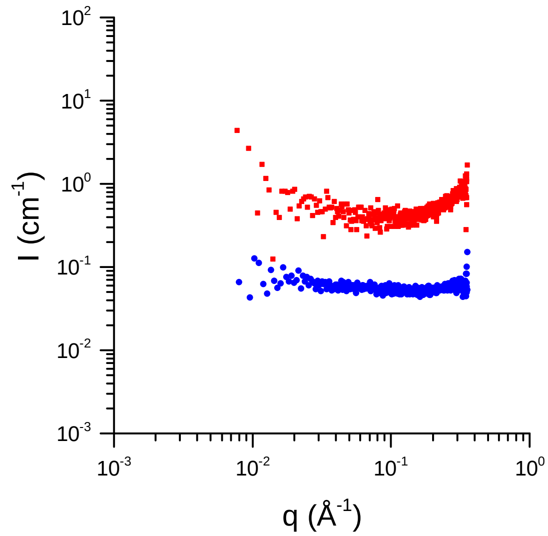

Figure 1: SAXS curves of aqueous phase before (blue squares) and after polymerization (red circles, $\times 10$)

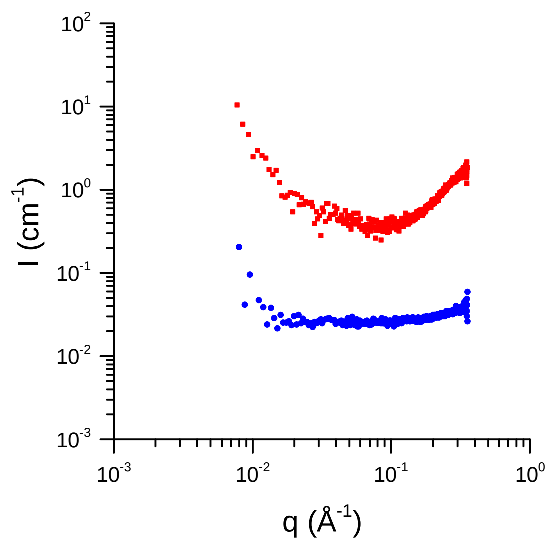

Figure 2: SAXS curves of organic phase before (blue squares) and after polymerization (red circles, $\times 10$)

Bragg peaks in the cubic bicontinuous phase

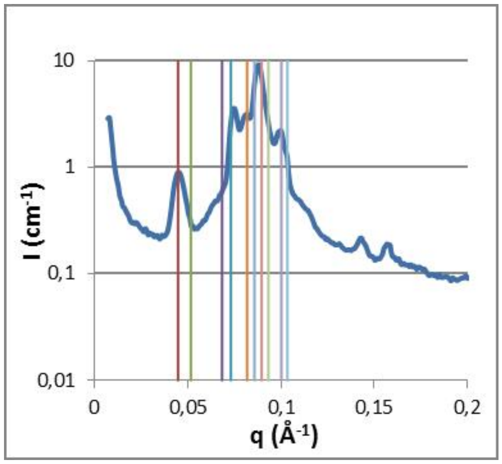

Figure 3: SAXS curves of BC sample before polymerization with Bragg peaks position of an Ia3d bicontiuous cubic structure: q_0, $\frac{2}{\sqrt{3}}q_0$, $\sqrt{\frac{7}{3}}q_0$, $2\sqrt{\frac{2}{3}}q_0$, $\sqrt{\frac{10}{3}}q_0$, $\sqrt{\frac{11}{3}}q_0$, $2q_0$, $\sqrt{\frac{13}{3}}q_0$, $\sqrt{5}q_0$, $\frac{4}{\sqrt{3}}q_0$... with $q_0 = 0.0448$ Å^{-1}

Models used for fitting SAXS curves

- *Form factor of monodisperse spheres* of radius R:

$$P(q) = A \cdot \left(\frac{3(\sin(qR) - qR \cdot \cos(qR))}{(qR)^3} \right)^2 \tag{1}$$

with the prefactor: $A = \bar{n}(l_T \cdot v\Delta\mu)^2$ with v the volume of the droplets, l_T the scattering length of a single electron ($2.81 \cdot 10^{-13}$ cm), $\bar{n}$ the numerical density of droplets, and $\Delta\mu$ the differential electron density between the oil droplets and water.

- *Form factor of polydisperse spheres* of radius R with a Gaussian standard deviation σ:

$$P(q) = A \cdot \frac{1 + (qR)^2 + (q\sigma)^2 - e^{-2(q\sigma)^2}(f_{\cos}(q) + f_{\sin}(q))}{(qR)^6} \tag{2}$$

where :

$f_{\cos}(q) = ((1+2(q\sigma)^2) - (qR)^2 - (q\sigma)^2) \cdot \cos(2qR)$, and $f_{\sin}(q) = 2qR(1+2(q\sigma)^2) \cdot \sin(2qR)$

with the prefactor: $A = 8\pi^2 \cdot \bar{n} \cdot (\Delta\rho)^2 \cdot R^6$, N being the number of objects, and $\Delta\rho$ the differential scattering length density between droplets and the continuous phase.

- *Structure factor for hard spheres interaction* of radius R_{HS} and volume fraction of interacting objects Φ_{HS}:

$$S_{HS}(q) = \frac{1}{1 + \frac{24 \cdot \Phi_{HS} \cdot G}{2 \cdot q \cdot R_{HS}}} \tag{3}$$

  where

  $G = \alpha \cdot \frac{\sin(a) - a\cos(a)}{a^2} + \beta \cdot \frac{2a\sin(a) + (2-a^2)\cdot\cos(a) - 2}{a^3} + \gamma \cdot \frac{-a^4\cos(a) + 4((3a^2-6)\cos(a) + (a^3-6a)\sin(a) + 6)}{a^5}$

  with $a = 2 \cdot q \cdot R_{HS}$, $\alpha = \frac{(1+2\cdot\Phi_{HS})^2}{(1-\Phi_{HS})^4}$, $\beta = \frac{-6\cdot\Phi_{HS}\cdot(1+\Phi_{HS}/2)^2}{(1-\Phi_{HS})^4}$ and $\gamma = \Phi_{HS} \cdot \alpha/2$

- *Teubner-Strey model* with correlation length ξ and period d:

$$I_{TS}(q) = \frac{A_{TS}}{1 - 2\left(\frac{Mq}{L^2}\right)^2 + \left(\frac{q}{L}\right)^4} \tag{4}$$

  where $L = \sqrt{\left(\frac{2\pi}{d}\right)^2 + \frac{1}{\xi^2}}$ and $M = \sqrt{\left(\frac{2\pi}{d}\right)^2 - \frac{1}{\xi^2}}$

  with the prefactor: $A_{TS} = \frac{8\pi(\Delta\rho)^2}{\xi\left(\left(\frac{2\pi}{d}\right)^2 + \frac{1}{\xi^2}\right)^2} \cdot \Phi(1-\Phi)$, Φ being the volume fraction of one phase, and $\Delta\rho$ the differential electron density between the aqueous and organic phases.

Electron contrast between aqueous and organic phases

The prefactor of the form factor found by fitting SAXS curve of OinW sample is:

$$A = \Phi \cdot v \cdot (l_T \cdot \Delta\mu)^2 = 0.32\ cm^{-1} \tag{5}$$

where:

- $\Phi = \Phi_{HS} \cdot (R/R_{HS})^3$ is the volume fraction of the oil droplets calculated from hard-sphere volume fraction (Φ_{HS}), hard-sphere radius (R_{HS}), and droplet radius (R)

- $v = 4/3 \cdot \pi \cdot R^3$ is the volume of one droplet
- $l_T = 2.8 \cdot 10^{-13}$ cm is the scattering length of a single electron
- $\Delta\mu$ is the electron contrast.

We can then determine the electron contrast between aqueous and organic phases:

$$\Delta\mu = 1.0 \cdot 10^{23} \text{ electrons/cm}^3$$

This value is consistent with the compositions of aqueous (water, AMPS and MBA) and organic phases (HMA and EGDMA).