ELECTRONIC SUPPLEMENTARY INFORMATION

Inner structure and dynamics of microgels with low and medium crosslinker content prepared via surfactant-free precipitation polymerization and continuous monomer feeding approach

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S1. Application of the Porod law to the SANS data

![Graph showing deviation of experimental data from the Porod law](image)

**Figure S1.** Deviation of the experimental data of batch-microgels (systems b-MGx) from the Porod law ($I(q) = Aq^{-\alpha}$) with exponent $\alpha$ of 4.

S2. X-ray small-angle scattering

X-ray experiments were performed on the diffractometer GALAXI (*Journal of large-scale research facilities*, 2, A61, 2016), operated by JCNS, Forschungszentrum Jülich, Germany. The wavelength of the GaK$\alpha$ line of $\lambda = 0.134$ nm was used. Cylindrical cells with a radius of 2.1 nm were used. An additional SAXS experiment was performed on the batch-microgel with 0.5 mol% BIS and 1.7 mol% initiator. Due to the small wavelength spread compared to SANS, features of the scattering curve are even more clearly seen (Figure S2). To fit this curve the same SiS model was used. As seen, the chosen model is in good agreement with experimental data, moreover fitting parameters $R$ and $r$ yield equal results for both methods (SANS and SAXS, see Table S2).

**Table S1.** Comparison of the fit parameters for system b-MG0.5 obtained from SANS and SAXS using the same SiS model. Fit errors are given in brackets.

<table>
<thead>
<tr>
<th>Method</th>
<th>$R$, nm</th>
<th>$r$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SANS</td>
<td>100 (0.01)</td>
<td>28.6 (0.002)</td>
</tr>
<tr>
<td>SAXS</td>
<td>101.4 (0.04)</td>
<td>29.1 (0.003)</td>
</tr>
</tbody>
</table>
**Figure S2.** SAXS curve of the microgel with 0.5 mol% BIS and 1.7 mol% initiator measured at 60°C (b-MG0.5). Line corresponds to the fit with SiS-model.

**S3. Internal domains concentration**

To estimate the concentration of the sub-domains (B) inside an individual microgel (A), presented in Fig. S3, further calculations were performed. The SiS model used for the fitting of the SANS and SAXS data of the batch-microgels at 50°C is:

\[
I(q, R, r) = I_A P(q, R) + I_B P(q, r) + I_{inc}
\]

where \( P(q, x) = \left[\frac{3\sin(qx) - qx \cos(qx)}{(qx)^3}\right]^2 \) is the form factor of spheres with a radius \( x \) (\( R \) or \( r \)), \( q = \frac{4\pi}{\lambda} \sin \theta \) – momentum transfer with neutron wavelength \( \lambda \) and scattering angle \( 2\Theta \), \( I_{inc} \) takes into account incoherent scattering.

Scaling parameters \( I_A \) and \( I_B \) are:

\[
I_i = \phi_i V_i (\Delta \rho_i)^2
\]  

(S3.1)

**Figure S3.** Spheres-in-sphere model visualization.
For individual particles:

\[ I_A = \varphi_A V_A (\Delta \rho_A)^2 \]  

(S3.2)

Where \( \varphi_A = n_A V_A / V \) is a particle volume concentration, \( n_A \) – a number of particles in a volume \( V \), \( V_A \) – a volume of the individual particle A. \( \varphi_{BinA} = n_B V_B / (\varphi_A V) \) is a volume concentration of domains B inside the particle A.

\[
\Delta \rho_A = \varphi_{BinA} \rho_B + (1 - \varphi_{BinA}) \rho_{D2O} \\
I_B = \varphi_{BinA} \frac{n_B V_B}{n_A V_A} V_B (\rho_B - \rho_{D2O})^2 = \varphi_{BinA}^2 V_B (\rho_B - \rho_{D2O})^2
\]  

(S3.3) (S3.4)

(S3.3) in (S3.2):

\[ I_A = \varphi_A V_A (\Delta \rho_A)^2 = \varphi_A \varphi_{BinA}^2 V_A (\rho_B - \rho_{D2O})^2 \]  

(S3.5)

\[ \frac{I_B}{I_A} = \frac{V_B}{V_A} \varphi_A \]

From (S3.5):

\[ \varphi_{BinA}^2 (\rho_B - \rho_{D2O})^2 = \frac{I_A}{\varphi_A V_A} \]

While \((\Delta \rho_B)^2 = (\rho_B - \rho_{D2O})^2\) is not exactly known parameter, the relation of the domain number to the particle number \( \frac{n_B}{n_A} = \varphi_{BinA} V_A / V_B \) was estimated at possible \( \Delta \rho_B \) (from previous investigations).

S4. VSANS of the batch- and feeding-microgels in low q-range.

Figure S4. VSANS spectrum of the batch- (A) and feeding-microgels (B) at 20°C in D\(_2\)O: 0.5 mol%BIS – red triangles, 2 mol%BIS – white squares, 5 mol%BIS – cyan circles. Lines correspond to the fits according to the function \[ I(q) = A / q^\alpha. \]
S5. Application of different models to ISF fitting process.

**Figure S5.** Comparison of a single exponential function (---) reported by Hellweg (*Coll. and Surf. A: Physicochem. and Eng. Asp.*, 2002) with a function including Zimm motion (—) for the system with 5 mol% BIS (A) and 0.5 mol% BIS (B) for selected $q$.

**Figure S6.** Application of the full Zimm model to the ISF of the f-MGx (A – 0.5 mol% BIS, B – 2 mol% BIS, C – 5 mol% BIS) and b-MGx (D – 0.5 mol% BIS, E – 2 mol% BIS) microgels. $q$ changes from $q_{\text{min}} = 0.041\text{Å}^{-1}$ (top curve) to $q_{\text{max}} = 0.19\text{Å}^{-1}$ (bottom curve).