Experimental report

09/02/2016

Proposal:	**9-10-1431**	**Council:**	4/2015
Title:	Polymer dynamics within microemulsion droplets		
Research area:	Soft condensed matter		

This proposal is a resubmission of 9-10-1401

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Samples: D2O / Polyethylenglycol
D2O / D-AOT / D-octane /

Instrument	Requested days	Allocated days	From	To
IN15	8	6	27/10/2015	02/11/2015
D11	1	0		
D33	0	1	21/09/2015	22/09/2015

Abstract:

Microemulsions, especially in the spherical phase, are a perfect system for the investigation of soft and hard confinement. The investigation of both simple liquids and polymer solutions in these confinements has so far been limited to the study of freezing behaviour or diffusional properties of the droplets. Using an appropriate deuteration scheme, neutron spin echo spectroscopy will now allow us to study the segmental dynamics of a confined polymer and to compare it to the polymer properties in solution. Together with our previous experiments on the surfactant dynamics of polymer loaded microemulsion droplets, we will obtain knowledge of the entire dynamics of this complex system: The diffusion of the droplet and the surfactant shell fluctuations are already investigated by us. Diffusional as well as segmental dynamics of the polymer within the droplets are the aim of this proposal.

Aim

Continuing our work on polymer loaded microemulsions based on the an-ionic surfactant AOT we focused on the structural and dynamical properties of the confined polymer Poly(ethylene oxide) (PEO) with a molecular weight of $1500\,\mathrm{g\,mol^{-1}}$. Within past experiments the soft confining geometry provided by the microemulsion was characterised by means of phase stability and its form fluctuations with small angle neutron scattering (SANS), backscattering (BS) and neutron spin echo spectroscopy (NSE). Results were discussed in experimental reports 6-02-403, 9-10-922, 9-10-1275 and publications [1–3]. In the present experiment an appropriate deuteration scheme using deuterated water, octane and AOT, keeping only the PEO protonated achieved a strong polymer contrast as distinguished from to the pronounced shell contrast in our past experiments. This contrast gave us the opportunity to directly investigate the conformation of the polymer in confinement and compare it to its bulk behaviour. Furthermore the polymer dynamics can be studied. In order to provide various confinement situations we prepared three different molar water to surfactant ratios $w = 15$, $w = 25$ and $w = 35$ resulting in droplet radii ranging from 20 Å to 53 Å with two different polymer concentrations, $Z = 1$ and $Z = 3$ polymer chains per droplet, each. In our previous investigations the radius of gyration of the polymer was determined to be 13 Å. Thus the microemulsions indeed provide a confining geometry to the polymer[3]. In order to separate confinement effects from the influence of different polymer concentrations the pure polymer water solution was investigated for several polymer concentrations as well.

Experimental details

The SANS measurements were performed on D33 with a wave length of $\lambda = 6$ Å and detector distances of 2.0 m and 5.3 m yielding a q range of $0.008\,\text{Å}^{-1} \leq q \leq 0.46\,\text{Å}^{-1}$. The raw data was radially averaged, corrected for electronic background and empty cell scattering, and normalized to the scattering from water using standard ILL software.

For the NSE experiments on IN15 we used neutron wave lengths of $\lambda = 8$ Å and measured at angles of 3.5°, 6.5° and 9.5°. The overall investigated q range was therefore $0.036\,\text{Å}^{-1}$ to $0.144\,\text{Å}^{-1}$ with Fourier times up to 72 ns. Instrumental resolution was determined with graphite which is a coherent elastic scatterer. All spectra were corrected for background scattering from fully deuterated microemulsion samples of according droplet radius without polymer and the sample holder. The multi-detector signal was sub-grouped into 3 q values per scattering angle.

For both experiments glass cuvettes were used as sample cells and the temperature was controlled to be 35 °C to ensure the stability of the droplet phase also for the polymer loaded samples.

Results

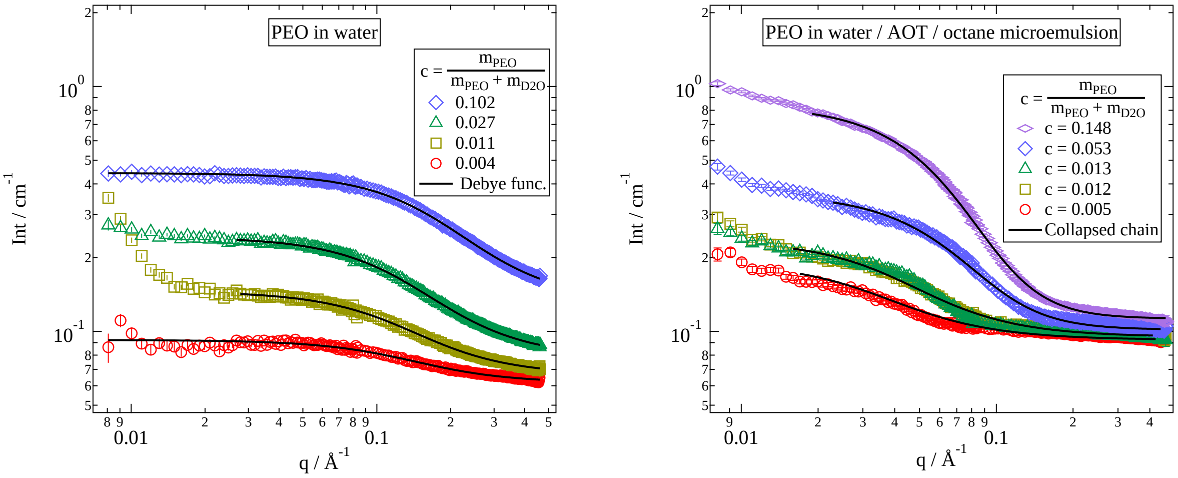

Figure 1: SANS data of the measured PEO in water (left) and PEO in microemulsion (right). Fitted models are described in the text

Small angle neutron scattering

The results of the SANS experiment on PEO in water and in the AOT based microemulsions are shown in figure 1. For the pure PEO water system the scattering curves can be well described by a Debye function implying a gaussian conformation of the polymer in solution[4]. The resulting radius of gyration is in accordance with our past experiments around $R_g = 13\,\text{Å}$. The situation completely changes when the confinement is introduced. The flat plateau at low q values changes into an increasing slope, while the prominent kink moved to lower q values. The Debye function is not longer capable to describe the data, thus a new model has to be introduced which allows for a variable Flory exponent ν[4, 5]:

$$I(q) = I_0 \frac{1}{\nu U^{\frac{1}{2\nu}}} \gamma\left(\frac{1}{2\nu}, U\right) - I_0 \frac{1}{\nu U^{\frac{1}{\nu}}} \gamma\left(\frac{1}{\nu}, U\right) \tag{1}$$

with

$$U = \frac{q^2 R_g^2 (2\nu + 1)(2\nu + 2)}{6} \tag{2}$$

The polymer properties are described by the radius of gyration R_g and the Flory exponent ν. The lower incomplete gamma function is given by $\gamma(s, x)$. If the Flory exponent is $\nu = 0.5$ the model reproduces the Debye function, $\nu = 0.6$ is the limit for an expanded chain and $\nu = 1/3$ for a collapsed one. As shown in figure 1 the scattering data of the confined polymer can be described by the fit model.

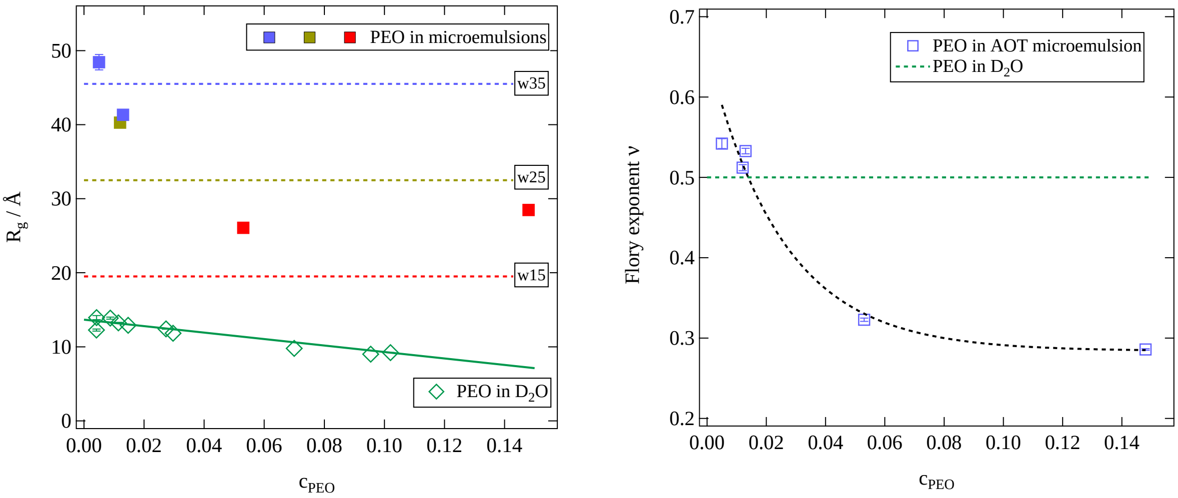

Figure 2: Left: Determined radii of gyration of the PEO and PEO in confinement fitted with the model described above. The dotted lines give the droplet radii thus the confinement size. The colour of the data points shows the associated confinement size. Right: Fitted Flory exponents.

The fit parameters R_g and ν are shown in figure 2. The first interesting observation is that all fitted radii of gyration a significantly larger than the ones measured in the pure PEO water system. However the precise confinement size seems not to play a significant role since a polymer concentration of $c_{\text{PEO}} = 0.013$ results in $R_g \approx 40\,\text{Å}$ independent from the size of the confining droplet. Secondly, the Flory exponents start around $\nu = 0.5$ and then decreases to approximately $1/3$ thus the local monomer structure becomes more dense. A possible explanation describing both observations is that polymer chains stick to the surfactant layer of the droplets covering the interface between water and surfactant[6–8]. Due to the attractive interaction between polymer and surfactant the single parts of the chain would try to get close to the wall thus making the polymer architecture more dense and spreading over a wider range increasing simultaneously the radius of gyration. Nevertheless the polymer radii of gyration should not exceed the droplet radius as is observed for most of our systems. This point is still under investigation.

Neutron spin echo spectroscopy

For the neutron spin echo experiments an exemplary data set is given for the PEO in microemulsion sample with $c_{\mathrm{PEO}} = 0.148$ in figure 3. The dashed lines are fits of a single exponential decay with an effective diffusion coefficient which describes the data quite accurate. The resulting q dependent diffusion coefficient for all investigated systems is depicted in the right part of figure 3.

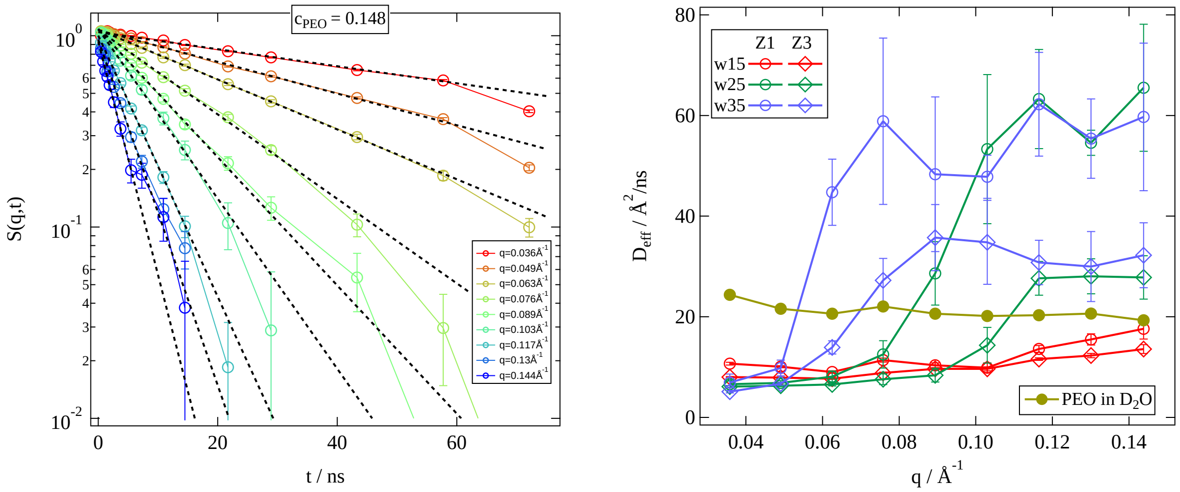

Figure 3: Left: Exemplary intermediate scattering function for the given concentration fitted with single exponential decays. Right: Resulting effctive diffusion coefficient for all PEO concentrations in microemulsions and a PEO water system.

It is neither constant as one would expect for a freely diffusing particle like PEO purely in water. Nor does it show the prominent peak at the position of the form factor minimum of the droplet what is usually observed for microemulsions with shell contrast (see e.g. report 9-10-922). Instead two regimes can be seen. At low q a constant value around $D_{\mathrm{eff}} = 8\,\text{Å}^2\,\mathrm{ns}^{-1}$ is observed which decreases with increasing droplet size and is comparable to the free diffusion of microemulsion droplets of according size[3]. At a characteristic q value, which depends on droplet size and polymer content, the effective diffusion coefficient increases and seems to reach a second plateau at even higher q values. Comparing the characteristic q value with the size of the droplets reveals that it corresponds well with the minimum of the form factor thus at lower q we should be sensitive to the dynamics of the droplet as a whole and for higher q we are capable to look insides the droplets dynamics. This brings us to the conclusion that at high q we observe the diffusion dynamics of the polymer in water combined with the over all droplet diffusion in the surrounding oil. The interesting fact that Z=1 and Z=3 systems seem to have the same plateau value at high q is still under investigation and can not be explained so far. A second difficulty are the rather large error bars for large droplets with low polymer concentration which is due to the low signal and the quite fast dynamics of the polymer. Therefore we try to refine our fitting procedure to further improve our results.

References

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