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# Supplementary Material: Polymer conformation changes in nanoscopic soft confinement

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## 1 Synthesis of deuterated AOT

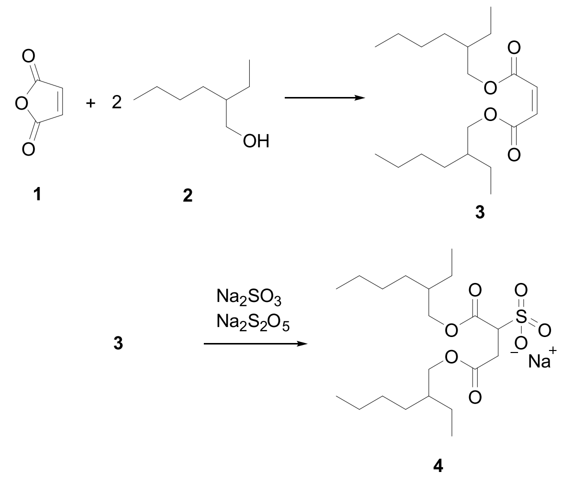

**Fig. 1** Synthetic scheme for the synthesis of deuterated AOT **4**

The two-step synthesis of deuterated AOT **4** is being carried out as depicted in scheme 1. The first step of the synthesis is the acid-catalysed esterification of maleic anhydride **1** with $d_{17}$-2-ethyl hexanol **2**. According to literature[1] 1.000 g (6.8 mmol) $d_{17}$-2-ethyl hexanol, 325 mg (3.31 mmol) maleic anhydride and 57 mg (0.33 mmol) p-toluenesulfonic acid were dissolved in 15 ml toluene and refluxed at 140 °C. The water is removed by a water trap for improving the yield. The reaction was monitored by TLC (petrol ether/ethyl ether 9:1). After completion, the mixture was cooled to 70 °C and transferred to the separating funnel at 70 °C. The organic layer was washed with a saturated solution of sodium bicarbonate and four times with water ($T = 70$ °C). Afterwards, the organic layer was diluted with a mixture of petrol ether and ethyl ether (9:1) and passed through a column filled with silica gel. The solvent of the filtrate was removed under reduced pressure and the product results as a yellow/brownish liquid with a yield of 93%. Purity was affirmed using $^1$H- and $^{13}$C-NMR-measurements (figure 2).

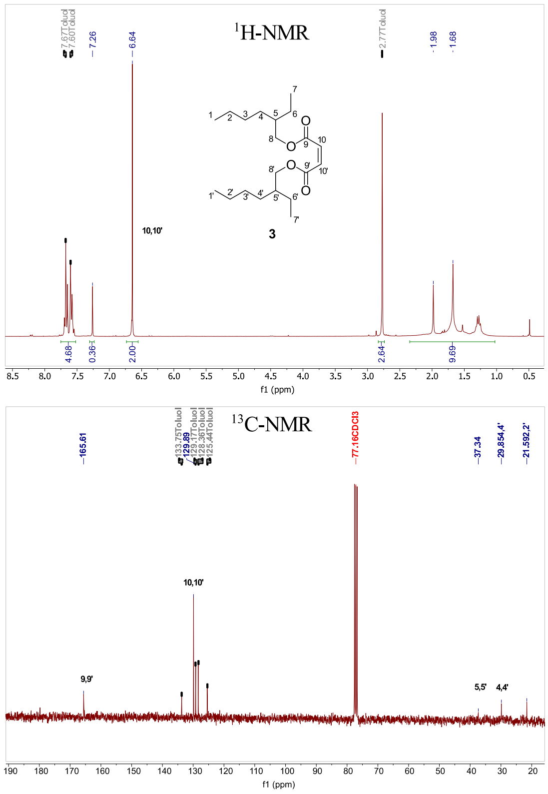

**Fig. 2** $^1$H-NMR-spectra of the deuterated ester **3** at 300 MHz in $CDCl_3$ (upper panel) and $^{13}$C-NMR-spectra of the deuterated ester **3** at 126 MHz in $CDCl_3$ (lower panel).

In the $^1$H-NMR-spectra the protons of the maleic acid compound can be found at a chemical shift of 6.64 ppm. Also small impurities can be found e.g. toluene at 2.77 ppm or small residues

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of the catalyst p-Toluenesulfonic acid (p-TsOH) ($< 2$ mol%). The $^{13}$C-NMR-spectra reveals e.g. the quaternary carbons of the deuterated ester **3** at 165.61 ppm and combined with the other signals in the spectra the success of the synthesis can be shown.

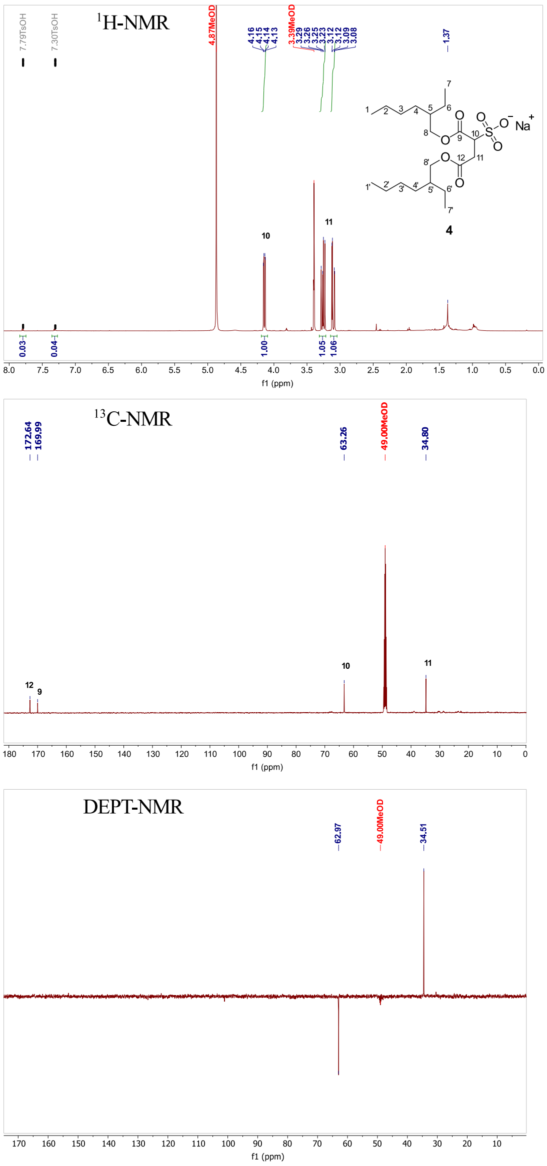

**Fig. 3** $^1$H-NMR-spectra (upper panel), $^{13}$C-NMR-spectra (mid panel) and DEPT-NMR-spectra (lower panel) of the deuterated AOT **4** at 500 MHz in methanol-d$_4$.

The sulfonation of the deuterated ester **3** is carried out with sodium sulfite and sodium metabisulfite according to scheme 1. 1.17 g (3.43 mmol) of the ester **3** are dissolved in 13 ml ethanol and 18 ml water. 740 mg (5.87 mmol) sodium sulfite and 1445 mg (7.60 mmol) sodium bisulfite are added to the solution and the resulting dispersion is stirred for 20 hours at reflux at 100 °C. The reaction was monitored by TLC (petrol ether/ethyl ether 9:1). Afterwards, the reaction was cooled to room temperature and the solvent was removed under reduced pressure. The resulting solid was dissolved in 25 ml ethyl acetate and the unsolvable residue was removed by filtration. The solvent of the filtrate was removed under reduced pressure and the residue was dissolved in as little methanol as possible. This (for the first run) turbid solution was centrifuged at 15 krpm for 15 minutes. The liquid phase was separated from the solid phase and the solvent was removed under reduced pressure. The centrifugation was repeated four times (until there was no more solid after centrifugation) leading to the deuterated product **4** with a yield of 74%. The purified deuterated AOT **4** could be obtained with a yield of 74%. The purity was affirmed using $^1$H-, $^{13}$C-NMR- and DEPT-NMR measurements (figure 3).

The NMR-spectra show the corresponding signals of the deuterated AOT **4**. The diastereotopic protons at carbon 11 show a sharp dd (doublet of doublets) peak multiplicity and overall there are only little impurities visible e.g. p-TsOH at a chemical shift of 2.5 and >7.5 ppm ($< 2$ mol%) which causes a little yellow discolouration.

In summary, the two-step synthesis of deuterated AOT **4** with an overall yield of 69 % was successful.

## 2 Guinier analysis

In the following figures the Guinier analysis of the SANS data from all investigated microemulsion samples is depicted. All scattering curves show a clear linear regime in this Guinier representation. Dashed line are fits to this Guinier regime.

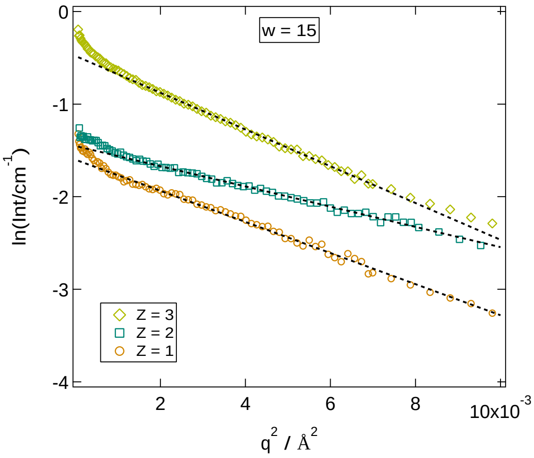

**Fig. 4** Guinier representation of the $w = 15$ samples with different average number $Z$ of polymer chains per droplet.

## 3 Properties of used substances

In the following two tables the important physical properties of the different components of the microemulsions are given. The different scattering length densities for neutrons and X-rays emphasize the complementarity of these two methods. For the surfactant scattering length densities of hydrophilic head group and hydrophobic tail group may vary significantly, thus these values are given separately.

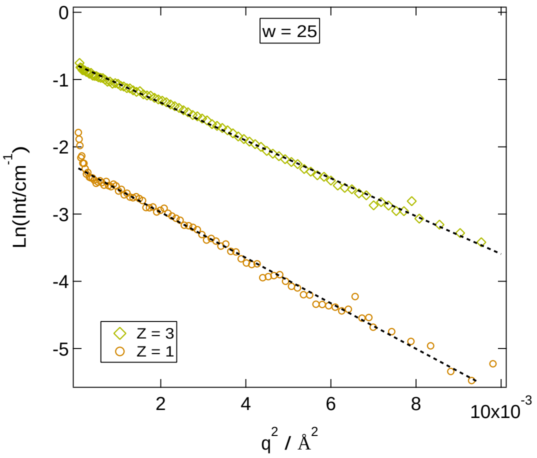

**Fig. 5** Guinier representation of the $w = 25$ samples with different average number $Z$ of polymer chains per droplet.

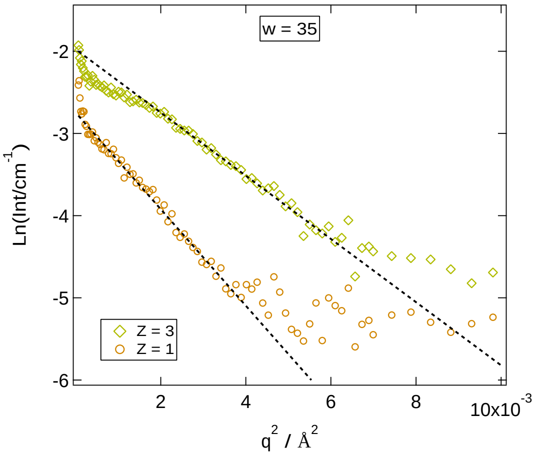

**Fig. 6** Guinier representation of the $w = 35$ samples with different average number $Z$ of polymer chains per droplet.

## References

1 K. Trickett, H. Brice, O. Myakonkaya, J. Eastoe, S. E. Rogers, R. K. Heenan and I. Grillo, *Soft Matter*, 2010, **6**, 1291–1296.

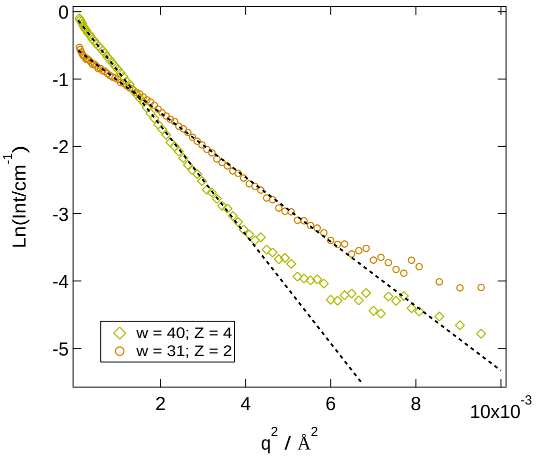

**Fig. 7** Guinier representation of the remaining samples with different molar water to surfactant ration $w$ average number $Z$ of polymer chains per droplet.

**Table 1** Components used for the formulation of microemulsions and their relevant properties. Scattering length densities (SLD) are calculated based on the chemical structure and density of the used substance by the *Scattering length calculator* from *NIST Center for Neutron Research*. For AOT, scattering lengths have to be given separately for the head and the tail group which is done in table 2

| molecule | $M/\mathrm{g\,mol^{-1}}$ | $\rho/\mathrm{g\,cm^{-3}}$ | $\mathrm{SLD_{Neut.}}/10^{-6}\,\text{Å}^{-2}$ | $\mathrm{SLD_{X\text{-}rays}}/10^{-6}\,\text{Å}^{-2}$ |
|---|---|---|---|---|
| $D_2O$ | 20 | 1.1 | 6.34 | 9.37 |
| D-AOT | 481 | 1.14 | - | - |
| $C_8D_{18}$ | 132 | 0.82 | 6.47 | 6.97 |
| $PEG_{1500}$ | 1500 | 1.2 | 0.68 | 11.14 |

**Table 2** Scattering length densities for different parts of deuterated AOT

| molecule | $\mathrm{SLD_{Neut.}}/10^{-6}\,\text{Å}^{-2}$ | $\mathrm{SLD_{X\text{-}rays}}/10^{-6}\,\text{Å}^{-2}$ |
|---|---|---|
| D-AOT head group | 7.02 | 23.8 |
| D-AOT tail group | 8.78 | 6.97 |