

Small Angle Neutron Scattering Instrument (KWS2)



Instrument Parameters

Beam tube:	NLIIB bent guide, cross section: 4.5 cm (height) $\times$ 3 cm (width)
Monochromator:	velocity selector; $\Delta\lambda/\lambda = 10\%$
Neutron flux at sample:	10^5 to 6×10^6 n/cm ² s depending on collimation; for 20 MW reactor power $\lambda = 7$ Å wavelength and entrance aperture of 3×3 cm ²
Collimation:	variable apertures at 1 m, 2 m, 4 m, 8 m, 14 m, 18 m, 20 m distance from sample opening width variable 0.5 ... 4.5 cm vertical opening width variable 0.5 ... 3.0 cm horizontal
Beam size at sample:	typically 1 cm $\times$ 1 cm
Detector - Active area: - Scintillator: - Space resolution: - Max. pulse rate: - Detection probability: - γ -sensitivity:	60 $\times$ 60 cm ² in 128 $\times$ 128 channels ⁶ Li-glass, 1 mm thickness 0.5 $\times$ 0.5 cm ² ca. 1 MHz ($\tau_{\text{dead}} = 3$ μ sec) 95 % for $\lambda = 7$ Å 2×10^{-4} (1 MeV)
Elastic Q-range:	$10^{-3} \leq Q/\text{\AA}^{-1} \leq 0.3$ (typically $2 \times 10^{-3} \leq Q/\text{\AA}^{-1} \leq 0.2$)
Sample environment:	evacuated sample chamber / open beam line cryofurnace 200 ... 500 K; shear cell of Searle type

Instrument Responsible

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Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-04-007		
Experiment title:	Small-angle neutron scattering studies of block copolymers adsorbed on perfluorocarbon emulsions		
Dates of experiment:	21.01.2005 – 25.01.2005	Date of report:	03.03.2006
Experimental team: Names	Addresses		
Terence Cosgrove Melissa Sharp Steve King	School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK CLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK		
Local Contact:	Martine Heinrich		

Experimental report text body

The conformation of adsorbed polymer or surfactant molecules in colloidal systems is of both fundamental importance and relevant to a wide range of technical systems. Our interest, in the pharmaceutical sciences, lies in the use of colloidal materials as drug delivery and targeting systems for the treatment of diseases as diverse as AIDS and cancer, the ultimate objective of this work is to develop means of directing drugs to a particular organ or cellular site, thus increasing their efficacy and reducing side-effects. Much recent work has centred on the use of adsorbed polymers to control the in vivo fate of drug-loaded colloidal particles. For example, it has been proven possible to select polymers to maximise vascular residence, or to cause preferential targeting of colloids to the bone marrow or the lymphatic system¹. Such targeting effects are primarily dependent on the nature of the surfactant, and are largely independent of the material from which the core of the particles is composed.

We have studied the interfacial layer structure of adsorbed polymers using light scattering, and have carried out some SANS experiments, in order to obtain greater detail. We use perfluorocarbon emulsions as the colloidal cores; these materials have the advantage that they can be contrast matched to their environment using approximately 72% D₂O in water. Perfluorocarbon emulsions can be made in a wide range of diameters from 80 – 1000 nm, of low polydispersity, with a wide range of adsorbed polymeric material. They are of pharmaceutical interest in their own right as oxygen transport media², and have been extensively studied as “artificial blood”. The polymers that were used to stabilise the emulsions were Pluronics, which are block copolymers, consisting of propylene oxide (PO) and ethylene oxide (EO), of the form (EO)_n(PO)_m(EO)_n. The emulsions used in this set of experiments had diameters of 294 nm and 319 nm when stabilised by, respectively, Pluronic F68 and Pluronic F127.

The small-angle neutron scattering experiments were carried out on instrument KWS-2 using sample-detector distances of 2m and 8m and a neutron wavelength of 6Å. This led to an approximate Q-range of 0.007 - 0.2 Å⁻¹. The emulsion concentration used for the majority of the measurements was 5 v/v %. The emulsions were stabilised by either Pluronic F68 or Pluronic F127. The emulsions were studied either off-contrast or where the oil phase was contrast matched to the water phase. This required approximately 72% D₂O. In addition to this the effect of salt was measured, using 0.2M NaCl solution. The effect of the emulsion concentration was studied, using emulsion concentrations of 10, 15 and 20 v/v %. All of these experiments were carried out both on and off contrast. Finally, we attempted to carry out the measurements contrast matching the polymer. This required approximately 16% D₂O. All measurements were carried out at 25°C.

The results obtained had a good signal to noise ratio. However, the data obtained contained peaks as a result of either a detector or a software malfunction. These peaks were not a result of the samples studied. We are still looking for a good way of dealing with this problem, and the data has therefore yet to be fitted.

A typical example of the data is shown in Figure 1 below. The sample measured is 5% emulsion stabilised by Pluronic F68, with the oil phase contrast matched.

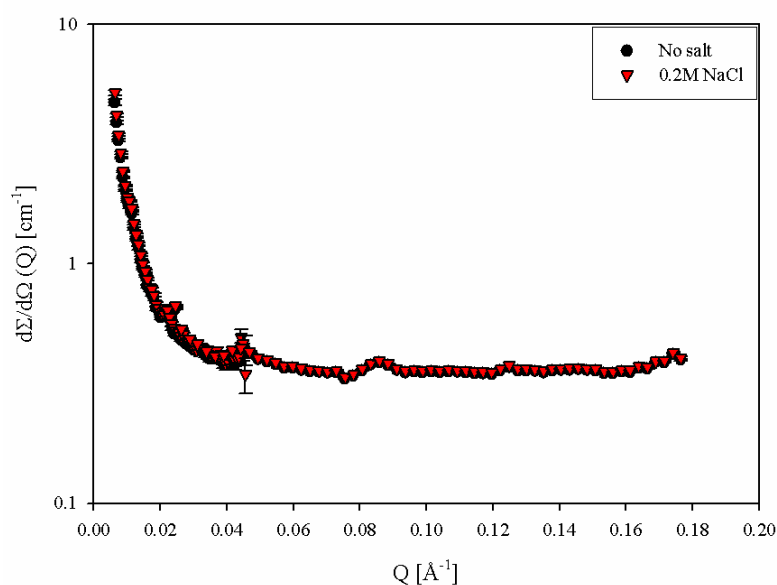


Figure 1

References

- (1) Illum, L.; Davis, S. S.; Muller, R. H.; Mak, E.; West, P. *Life Sciences* **1987**, *40*, 367.
- (2) Krafft, M. P. *Advanced Drug Delivery Reviews* **2001**, *47*, 209-228.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-04-008		
Experiment title:	Characterization of deformed and undeformed Al-alloys		
Dates of experiment:	19.-20.01.2006	Date of report:	22.06.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus Andreas Ulbricht Frank Bergner	Institut für Festkörperforschung, Forschungszentrum Jülich GmbH Forschungszentrum Rossendorf e.V. Forschungszentrum Rossendorf e.V.		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Background

The evaluation of safety and integrity of mechanically loaded structures such as the fuselage of commercial aircraft is based on fracture and damage mechanics concepts. In damage mechanics a damage function as well as damage parameters are needed in order to predict the mechanical behaviour of the component. SANS measurements offer the possibility to detect microstructural changes (including damage and evolution of the dislocation network) on the nanometer size scale while probing volumes much larger than grain size. Crystal dislocations are believed to cause rather weak SAS contrast for both X rays and neutrons. It was therefore surprising to observe, in a preliminary investigation, a strong deformation-induced anisotropy of contrast in specimens of thin-sheet wrought Al-Mg-Si alloy AA6013T4 deformed in tension up to uniform elongation. The aim of the present experiment was to reproduce the effect of deformation using optimized experimental conditions for both the naturally aged alloy (T4) investigated before and an artificially aged condition (T6) of the same alloy. The comparison of the two aging conditions should enable us to contribute to the understanding of the mechanism of deformation-induced contrast.

Experimental setup

The SANS experiment was carried out with a beam diameter of 10 mm and a neutron wavelength of 0.53 nm. Three different sample detector distances (14 m, 4 m and 1.25 m) and corresponding collimation lengths were used to measure scattering intensities with a scattering vector, Q , approximately ranging from 0.02 to 1.2 nm⁻¹. In order to enhance statistics, a number of six segments of 1.6 mm thick tensile specimens were placed front to back to form one compound sample for each condition. The compound samples of both undeformed and uniformly stretched material of 6013T4 (uniform elongation 18.5%) and 6013T6 (uniform elongation 7.5%) were exposed to the same experimental conditions to ensure optimum comparability.

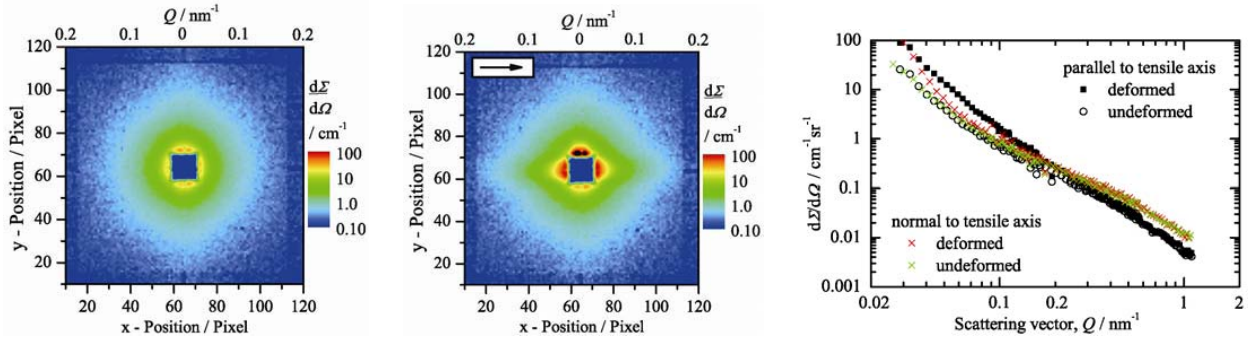


Fig. 1. SANS images of undeformed (left) and uniformly stretched Al alloy 6013T4 with the tensile direction indicated by an arrow (middle), scattering curves for Q vector parallel and normal to tensile axis (right).

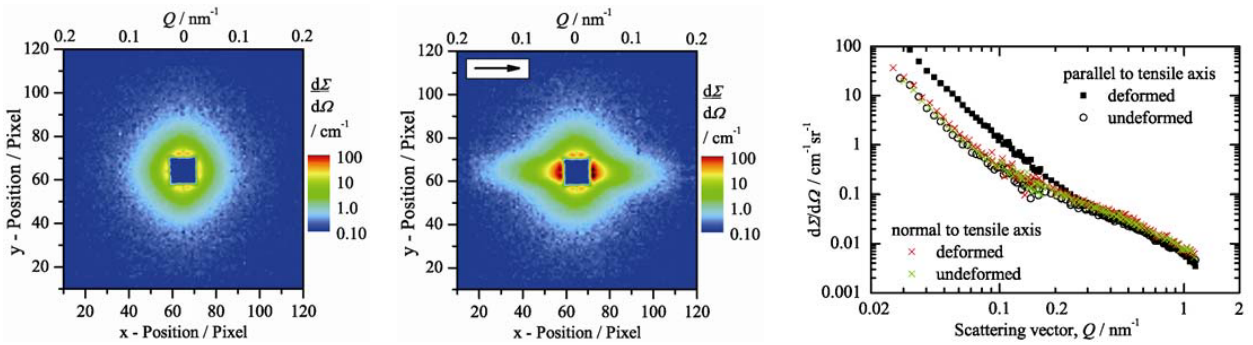


Fig. 2. SANS images of undeformed (left) and uniformly stretched Al alloy 6013T6 with the tensile direction indicated by an arrow (middle), scattering curves for Q vector parallel and normal to tensile axis (right).

Results

We are interested in the deformation-induced change of both scattered intensity and anisotropy. Two-dimensional patterns of the SANS intensities measured in the Q -range up to 0.2 nm^{-1} are shown in figures 1 and 2 for Al-alloy 6013T4 (aged at room temperature) and 6013T6 (aged at 190°C), respectively. The same colour scaling is used for the intensity in both figures. Scattering curves corresponding to the horizontal (Q parallel to tensile axis) and vertical (Q perpendicular to tensile axis) sections through the centre of the patterns are placed on the right hand side of these figures.

The following findings can be extracted from the experimental results:

- The in-plane scattering anisotropy of the undeformed thin-sheet materials is weak for both conditions.
- For the naturally aged condition T4 there is a pronounced deformation-induced increase of anisotropy, which basically agrees with the result of the preliminary measurements mentioned above.
- The same type of anisotropy is even more pronounced for the artificially aged condition T6. This is surprising, because the uniform elongation applied to these specimens (7.5%) was much smaller than for condition T4 (18.5%).
- At increasing Q -values the scattering curves for the undeformed and the stretched material cross one another in the case of T4 and approach one another in the case of T6.

It is well known that the contrast caused by single dislocations strongly depends on the type and orientation of the dislocation relative to the neutron beam and to the Q -vector. We therefore assume that the deformation-induced increase of anisotropy is caused by the formation of special arrangements of dislocations. The effect of the initial microstructure on the evolution of the dislocation network has to be considered in order to explain the observations summarized above on a quantitative basis. In any case, 2D SANS patterns are an extremely sensitive means to detect effects of anisotropy in plastic deformation.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-04-018		
Experiment title:	Performance of new Couette rheometer – Measurement of shear induced deformation of star-like micelles		
Dates of experiment:	28.01. – 01.02.2005	Date of report:	24.05.2006
Experimental team: Names	Addresses		
G. Rother, J. Stellbrink, L. Willner, D. Richter	Forschungszentrum Jülich, Institut für Festkörperforschung Forschungszentrum Jülich, Institut für Festkörperforschung Forschungszentrum Jülich, Institut für Festkörperforschung Forschungszentrum Jülich, Institut für Festkörperforschung		
Local Contact:	Dr. H. Frielinghaus		

Experimental report text body

The experiment aimed to test the installation and operation of the new Rheowis rheometer in the KWS environment.

The installation of the instrument on the standard sample table was possible using a special adapter plate. The rheometer is designed to operate at high rotational speed, we measured up to shear rates of 8000 Hz successfully. For the future even 10.000 Hz might be possible, but require some small improvements in the instrument. We studied the scattering from several diluted and concentrated samples of protonated and deuterated PEP1-PEO20 in water and water/DMF mixtures.

So far we measured the shear behaviour of the structure factor of h-PEP1-h-PEO20 at a volume fraction of 3%. With increasing shear rate a shift of the peak position to lower Q has been observed. The origin of this effect is not fully understood yet. Secondly the shear behaviour of the form factor of PEP1-PEO under zero average contrast conditions has been studied. The results of this measurement are shown in Figure 2. We found a decrease of the scattering intensity at low Q with increasing shear. Further evaluation of this complex system is necessary to obtain a comprehensive picture of the structural effects of shear appliance to that colloidal system. For the forthcoming experiments the electronic setup will be improved. The analysis of the data is underway.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-04-020		
Experiment title:	Interactions in concentrated sterically stabilized colloidal dispersions		
Dates of experiment:	6 to 9-Mar-2005	Date of report:	2-Mar-2006
Experimental team: Names	Addresses:		
Dong Qiu Yuan Wang Terence Cosgrove	School of Chemistry University of Bristol Cantock's Close Bristol BS8 1TS UK		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

Experimental report text body

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The stability of colloidal dispersions depends on the inter-particle interactions. Colloidal dispersions can be stabilized by electrostatically or sterically repulsion or both¹. The steric repulsion can be imparted by both physically adsorbed and surface grafted polymer chains in good solvents. We have already studied the steric interaction by physically adsorbed polymer chains^{2, 3}. In this study, we used the polystyrene latex with grafted PEO chains as a model system. The latex was synthesized by incorporating PEO macromonomer (PEO 1000 Mw) with styrene monomer during the emulsion polymerization process. Latex samples were dispersed in D₂O/H₂O mixture to make the PEO layers invisible. Therefore, a simple spherical form factor is applicable. 20 mM NaCl was present to screen the electrostatic repulsion caused by surface charges.

Figure 1 shows the scattering spectra. Surprisingly, no structure factors were found even for concentrated samples (0.13 volume fraction). All the data can be perfectly fitted by a hard-sphere form factor, the results are shown in Table 1. It can be seen that these latex particles are very monodisperse and they are very stable against electrolyte. They did not flocculate even in presence of 0.1 M NaCl.

The good stability of these colloidal particles against electrolyte implies the presence of an effective PEO layer on the particle surface. These layers seem to be very thin (no structure factor). However, they can provide a considerably high energy obstacle to keep the particles apart against van der Waals attraction. These latex particles can be a perfect model for studying hard-sphere behaviors. Regretably, we did not observed the steric interaction by SANS directly, but their behavior in ionic environment supports such an interaction. Considering the short length of the PEO chains, the steric interaction could be expected to be short range. A higher volume fraction or longer grafted polymer chains may be needed for such an effect. This is part of our ongoing work.

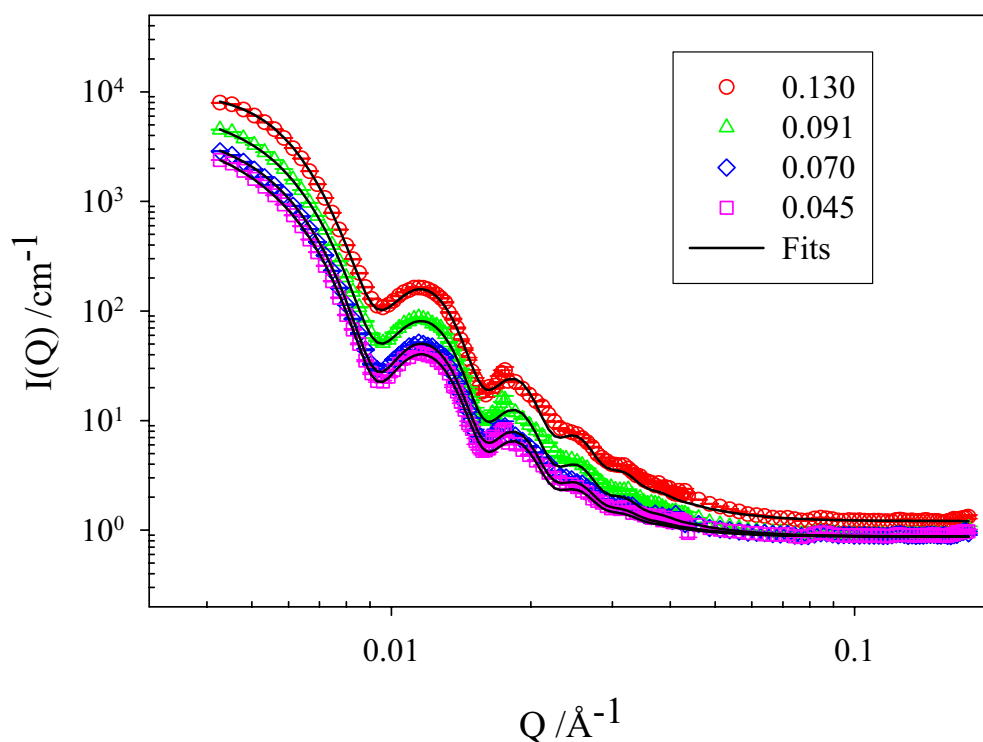


Figure 1. The SANS spectrums of polystyrene latex with grafted PEO at different volume fractions.

Table 1. Parameters used to fit the experimental data in Figure 1.

Volume Fraction	0.130	0.091	0.70	0.045
Particle Radius (Å)	480 ± 2	478 ± 2	477 ± 2	477 ± 2
Polydispersity	0.06	0.06	0.07	0.07

Reference:

1. Hunter, R. J., *Foundation of Colloid Science*, Clarendon Press: Oxford, **1987**; Vol. I.
2. Qiu, D.; Cosgrove, T. *Experimental report for KW1-03-013*, 2005.
3. Qiu, D.; Dreiss, C.A.; Cosgrove, T.; Howe, A. M. *Langmuir*, **2005**, 21, 9964..

Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-04-021		
Experiment title:	Microstructure and magnetic interactions in FeAg granular thin films		
Dates of experiment:	10-14 May 05	Date of report:	1 Jun 06
Experimental team:			
Names:	Addresses:		
Ana García Prieto	Dpto. Electricidad y Electrónica, UPV-EHU, Apartado 644, 48080 Bilbao, Spain		
Gustavo Sarmiento	Dpto. Electricidad y Electrónica, UPV-EHU, Apartado 644, 48080 Bilbao, Spain		
Local contact:	Henrich Frielinghaus		

Small Angle Neutron Scattering (SANS) experiments were performed on $\text{Fe}_x\text{Ag}_{100-x}$ ($x = 6, 15, 25, 31, 49$) granular thin films. The films, of thicknesses ranging between 80 and 150 nm, were prepared by laser ablation and lay over a Si substrate of $\approx 250\mu\text{m}$ thick.

SANS experiments on granular samples can provide evidence of the existence of very small Fe clusters that otherwise are very complex to detect by XRD or TEM due to their small size (≈ 4 nm). Moreover, magnetic information can be obtained due to the magnetic character of the Fe clusters.

Previous magnetic and magnetotransport measurements on these samples show that for $x \leq 25$ the magnetic response is superparamagnetic-like, with no coercivity and remanence and not saturated hysteresis loops at 300 K. From Langevin fits of the hysteresis loops a cluster size of 4 nm has been estimated. As the Fe concentration increases ($x > 25$) the loops lose their superparamagnetic character: coercivity and remanence appear suggesting a new ferromagnetic-like regime with a prevalence of exchange coupling over the dipolar interactions [1, 2].

Regarding the magnetotransport response of the samples, all of them show Giant Magnetoresistance (GMR) when the magnetic field is in the sample plane and Extraordinary Hall Effect (EHE) when is perpendicular for $x \geq 25$, this anisotropic response being due to the planar shape of the Fe clusters. The SANS experiments were made at room temperature in transmission configuration. Four different detector distances were used in order to cope with a suitable range in Q , from 0.003 to $0.34 \text{ \AA}^{-1}$ with $\lambda = 5.3 \text{ \AA}$.

Results of the SANS measurements performed at KWS-2 are shown in Figure 1.

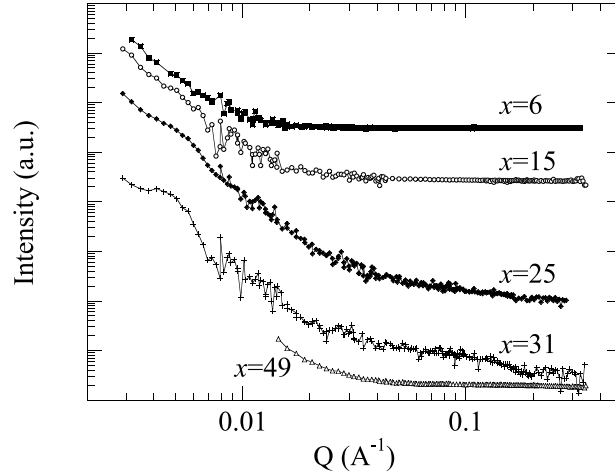


Figure 1: SANS measurements performed at KWS-2 for $\text{Fe}_x\text{Ag}_{100-x}$ ($x = 6, 15, 25, 31, 49$) thin films.

From a qualitative analysis of the curves, the samples with $x < 25$ show a similar shape, with a steep decrease of the intensity at low Q followed by a plateau. For $x > 25$ there is a shoulder at low Q and a slower decrease of the intensity up to the highest Q . This could be a fingerprint of the magnetic transition at $x = 25$ inferred from the analysis of the hysteresis loops.

From fittings of the curves at high Q (Porod region) we have found that the Fe-Ag interface is mainly not sharp, which suggests that there could be some atomic substitution between the two species. However, fittings of the low Q region to a Guinier law result in particle sizes inconsistent with the ones extracted from the magnetization loops. Further numerical studies are being performed by a complex analysis consisting on fitting the curves to a spherical form factor under the Perkus-Yevik approximation for hard spheres. From this procedure we expect to complete the information on the sizes, size-distribution and concentration of the magnetic nanoparticles as a function of Fe concentration.

References

- [1] *Magnetic and magnetotransport behaviour of granular $\text{Fe}_x\text{Ag}_{100-x}$ thin films*, G. Sarmiento, M.L. Fdez-Gubieda, I. Orue, J. Magn. Magn. Mat., accepted
- [2] *The role of the interface on the magnetic behaviour of granular $\text{Fe}_{50}\text{Ag}_{50}$ film*, M.L. Fdez-Gubieda, G. Sarmiento, L. Fernández-Barquín, I. Orue, J. Magn. Magn. Mat., accepted



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-04-022, KW2-05-032		
Experiment title:	Test of a polarized neutron setup at KWS-2		
Dates of experiment:	03.10. – 04.10.2005	Date of report:	13.06.2006
Experimental team: Names	Addresses		
E. Kentzinger H. Frielinghaus A. Ioffe M. Feygenson Th. Brückel	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	H. Frielinghaus		

Experimental report text body

The aim of this experiment was to check whether one could obtain a polarized beam at KWS-2 by installing a polarizer at sample position and whether this primary beam could be kept clean from any small angle scattering from this polarizing device.

The drawing and the picture of Fig.1 explains the set-up:

- 1) The polarized neutron beam was produced using a Fe/Si supermirror device working in transmission. In that way, the direction and the collimation properties of the beam were not affected. Previous measurements have shown that the small angle scattering of such a supermirror is relatively weak, provided that the supermirror is put in a large enough field (see report HAD-04-018).
- 2) The projection of the spin on the quantization axis was changed by using a radio-frequency spin flipper. The main advantages of the use of such a spin flipper at a SANS machine are that there is no material into the beam (therefore no scattering is produced by this device), and that it can flip neutrons over a relatively wide wavelength spectrum range. At the exit of the flipper, an absorber plate was installed (B_4C powder on Cd) in order to absorb the + neutrons specular reflected by the polarizer.
- 3) The polarization of the thus obtained neutron beam and the flipping ratio of the flipper were tested by studying the reflection of spin-up and spin-down neutrons by a FeCoV/TiN polarizing supermirror.

The results are shown in Fig.2 which shows measurements performed at C8-D3. A relatively clean empty beam was obtained. In following experiments, the intensity around the empty beam was better suppressed by replacing the absorber plate at the exit of the flipper by a slit.

The polarization efficiency was analyzed by installing a polarizing supermirror in a remanent state after the flipper. In that state, this device mainly reflects spin-down neutrons. From the bottom part of Fig.2, we can deduce a flipping ratio of the whole set-up equal to 35, big enough to perform polarized GISANS experiments.

Sample slits of KWS-2

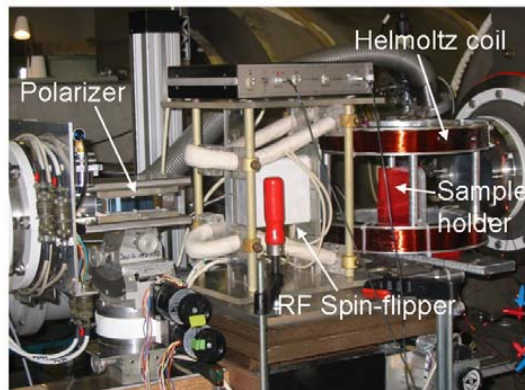
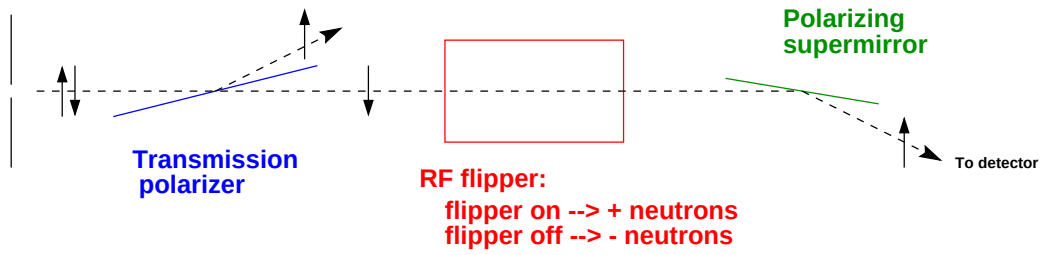


Fig. 1: Sketch and photo of the set-up used at KWS-2 to measure polarized GISANS from a polarizing supermirror.

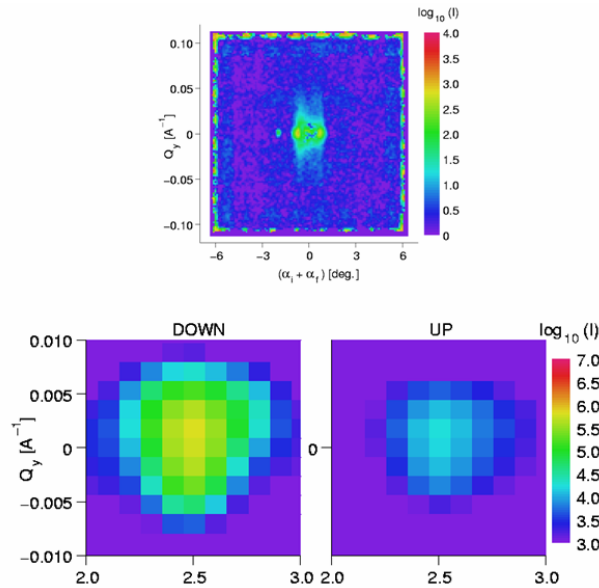


Fig. 2: Top: 'Empty beam' of the polarized neutron experiment. Bottom: Spin down and Spin down reflectivity of the supermirror in its remanent state at an angle of incidence set close below the effective angle of total reflection.



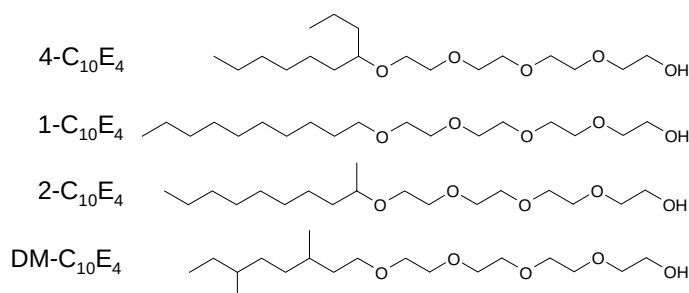
Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-001		
Experiment title:	Non-ionic surfactants with different alkyl-chains		
Dates of experiment:	05.03.2005 – 06.03.2005 10.03.2005 – 11.03.2005 09.04.2005 – 11.04.2005	Date of report:	09.03.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus Christian Frank Simona Maccarrone Jürgen Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Non-ionic surfactants with different alkyl-chains

Technical C₁₀E₄ surfactants have been synthesized by ethoxylation of different decanols. The various isomers 4-decanol, 1-decanol, 2-decanol and di-methyl-octanol lead to a branched structure of the hydrophobic alkyl-block. These branched surfactants are very interesting in applications, but have never been investigated systematically. Here, we studied 4 microemulsions of D₂O, decane, and one of the C₁₀E₄ surfactants. Phase diagrams were determined and compared to the SANS measurements we present here.



Scheme 1: Chemical structures of the 4 surfactant molecules. They were synthesized from different decanols by ethoxylation. The alcohols were 4-decane, 1-decane, 2-decane and an octanol with two methyl side groups.

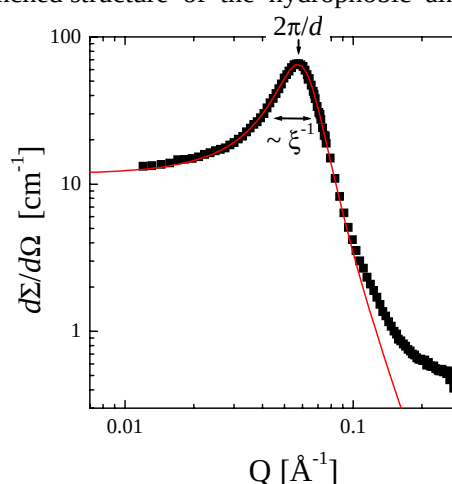


Figure 1: Typical SANS pattern of the surfactant 4-C₁₀E₄. Red curve is a fit to the Teubner-Strey theory. The obtained parameters are the domain size d and the correlation length ξ .

A typical SANS pattern is shown in figure 1. A correlation peak appears, the position of which is connected to the domain size d , and the width of which is inversely proportional to the correlation length ξ . A more refined description is achieved by a fit of the Teubner-Strey formula [1]. At larger scattering angles Q deviations occur due to (a) the lack of describing the true surface (true Porod constant is larger), and (b) due to the incoherent background which has not been subtracted so far.

The obtained parameters d and ξ are plotted as a function of the membrane volume content Ψ in figure 2. The domain size measures the average distance of two consecutive domains, and therefore is twice as large as the correlation length. The domain size can be described by a theory of Roux [2]. Roughly the domain size is inversely proportional to the membrane content, but in the refined model a logarithmic correction takes care of the membrane fluctuations which lead to a larger surface compared with the planar membrane. The theory describes the measured domain size well with a single parameter, the film thickness δ .

The so obtained film thickness δ is shown as a function of the surfactant molecule in figure 3. For the last three surfactants 1-C₁₀E₄, 2-C₁₀E₄, and DM-C₁₀E₄ the backbone length seems to have direct influence on the film thickness. The highly pure 1-C₁₀E₄ has a film thickness of 12.0 Å. Our technical 1-C₁₀E₄ has a little longer ethylene oxide chain which explains the larger δ of 14.7 Å. It is known that the surfactant molecules are strongly tilted by 66° relative to the normal axis of the membrane. The reduction of one backbone carbon therefore would lead to a reduced film thickness by 0.52 Å. The regression line represents this slope well. Thus, the film thickness of the 3 surfactant molecules is not influenced by the branching. The branching influence is much higher for the 4-C₁₀E₄ surfactant since the branch is 3 carbons long. A change of the tilt angle might be an explanation.

The bending rigidity κ is obtained by the structural parameters by the Gaussian random field theory which predicts $\kappa \sim \xi/d$. Comparing the phase diagrams (not shown here) with the bending rigidity one finds: The lower the minimal surfactant concentration (fish tail point) is the larger the bending rigidity is. Obviously a more rigid membrane leads to larger structures with a better surface to volume ratio. The largest κ is obtained by the normal 1-C₁₀E₄. The next lower κ is obtained by DM-C₁₀E₄, which obviously has the smallest perturbation of the branching since the methyl groups have the largest distance to the hydrophilic head. The other two surfactants 2-C₁₀E₄ and 4-C₁₀E₄ have the branching directly connected at the hydrophilic head. The shorter side group leads to the next lower κ , while the relatively large side group leads to the lowest κ .

We therefore could explain the film thickness and the surfactant efficiency (and κ) by the molecule structure.

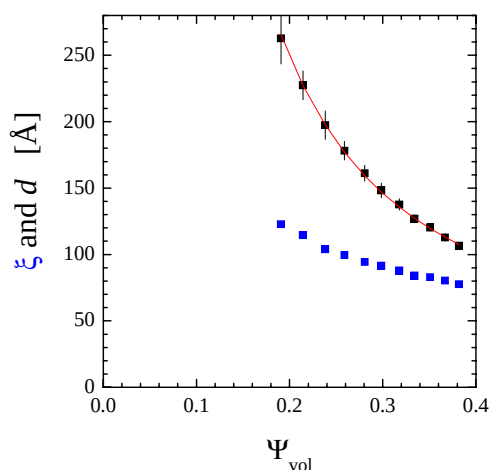


Figure 2: The domain size d and the correlation length ξ obtained by the Teubner-Strey fit to the SANS measurements as a function of the membrane content Ψ . The fitted line is due to the theory of Roux [2].

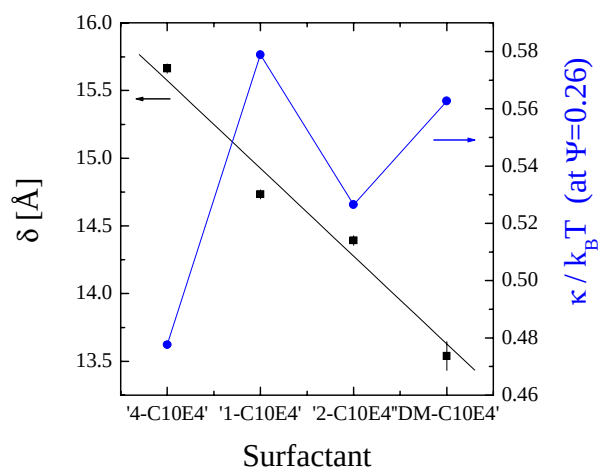


Figure 3: The film thickness δ obtained by the description of the domain size d by Roux's theory [2]. The bending rigidity κ is read off at a constant membrane content $\Psi = 0.26$.

References:

- [1] M. Teubner, R. Strey, *J. Chem. Phys.* **87**, 3195 (1987)
- [2] D. Roux, F. Nallet, E. Freyssingeas, G. Porte, P. Bassereau et al., *Europhys. Lett.* **17**, 575 (1992)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-002, KW3-05-001		
Experiment title:	Self-assembling behavior of crystalline/amorphous random copolymers in dilute solutions: 3-segments PEB-6.5/8.9/10.1 and 4-segment PEB-2.6/6.0/10.9/13.2 in decane studied with SANS (parts 2 and 3)		
Dates of experiment:	12.04.05 – 15.04.05 17.05.05 – 23.05.05	Date of report:	29.05.06
Experimental team:			
Names	Addresses		
Aurel Radulescu, Emmanuel Kentzinger, Jörg Stellbrink,	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.H.Frielinghaus, Dr.E.Kentzinger		

Experimental report text body

The self-assembly of poly(co-olefins) in dilute solution has been shown via SANS to yield either plate-like or needle-like micelles-like micelles [1,2]. The resultant supramolecular structures are dependent upon the copolymer architecture. The crystalline-amorphous diblock co-polymers yield self-assembled hairy plates while the corresponding random co-polymers yield one-dimensional needle shaped aggregates. Both kinds of polymers are able to modify the wax crystal structures in dilute solution. The diblock copolymers form a 2-d morphology consisting of a crystalline core surrounded by amorphous brushes. The core nucleates the wax crystals while the brush keeps them small and prevents their 3-d development. The PEB- n random copolymers (n - the number of ethyl sides per 100 backbone carbons) show selectivity in their wax crystal modification capacities depending on their crystallinity that is tuneable by n , i.e. the lower n the higher the crystallization tendency and the higher the temperature at which it initially occurs. By SANS and rheology [2] it was stated that efficient PEB- n additives for oil industry would contain graded ethylene content. Therefore, a SANS study of the self-assembling morphology in solution and wax crystal modification capacity of multi-segment random copolymers presenting graded ethylene content was initiated recently [3]. The study focused on two multi-segment copolymers, a triblock PEB-6.5/8.9/10.1 and a tetrablock PEB-2.6/6.0/10.9/13.2 and reported about the temperature behaviour of the self-assembling properties of these materials in decreasing temperature from the single coil regime (85°C) up to 0°C. The present experiments continued the structural study of the polymer aggregates formed at temperatures below 0°C and extended the investigation to a larger length scale by involving the focusing-SANS technique. In this way structures showing characteristic sizes from 1 μm to 1 nm formed upon cooling in solutions of multi-block random copolymers could be characterized. The conventional SANS investigations performed at -10°C and 0°C revealed that the scattering patterns do not change qualitatively in comparison with those collected at temperatures above 0°C and quantitatively show a continuous increase of the scattered intensity level. One can roughly conclude that the morphology of the

aggregates formed by multiblock random copolymers in solution does not change only their number increases in decreasing temperature. Fig.1 shows the scattering patterns from the structures formed by the two investigated multi-block copolymers at -20°C in decane. These present most likely a 1-dimensional morphology as it is revealed by the Q^{-1} power law behavior of the scattering at low Q . The 1D morphology must be formed by core-shell crystalline-amorphous substructures as long as the highly crystallizable PEB-2.6, PEB-6.0 and PEB-6.5 blocks should form compact crystalline objects. The focusing-SANS (F-SANS) investigations have been stimulated by the microscopy observations revealing large-scale aggregates with sizes in the range of micrometers formed by the multi-block copolymers in solution. Fig.2 presents the joined conventional-SANS and F-SANS scattering patterns: it seems that the 1D crystalline-amorphous objects associate and form soft spherulitic-like aggregates with radii ranging between 1.5 μm as in case of the tri-block material (Beaucage analysis of the F-SANS data for a power law of Q^{-4} [4]) and 5 μm as for the tetra-block material (revealed by the micrographs, Fig.3). The analysis of the structural and density parameters of these morphologies in terms of models and the elucidation of the contradictory Q^{-4} behavior of the scattering from soft structures as those revealed by microscopy is in progress.

References: [1] D.Richter et al., *Macromolecules* 30, 1053, 1997; [2] H.S.Ashbaugh et al., *Macromolecules* 35, 7044, 2002; [3] experimental report KW1-04-026 FRJ-2; [4] G.Beaucage, *J.Appl.Cryst.* 29, 134, 1996.

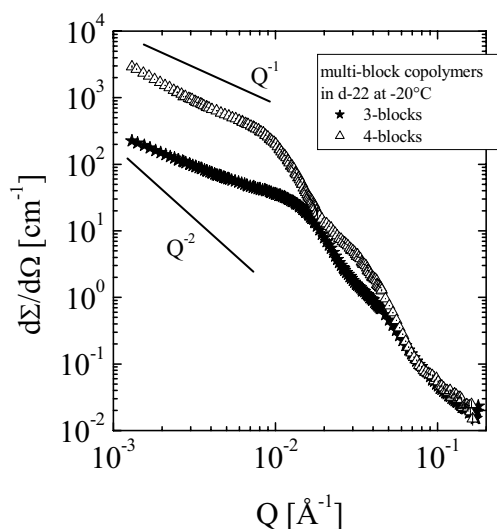


Fig.1 – Conventional SANS patterns from multi-block random copolymers. The Q^{-1} power-law behaviour of the scattering at low Q is obvious.

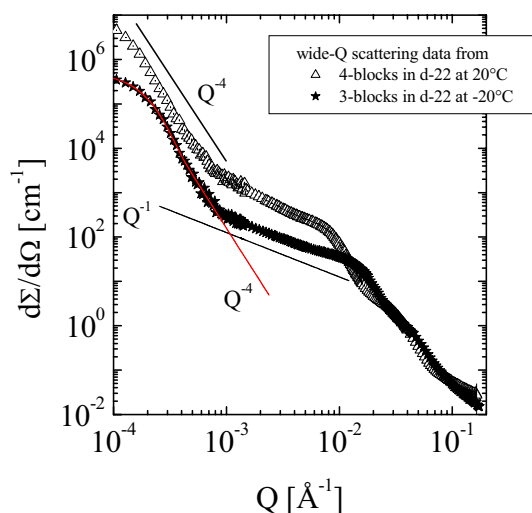


Fig.2 – Wide-Q scattering patterns from multi-block random copolymers. The Beaucage analysis of the scattering at low Q is depicted by the red curve.

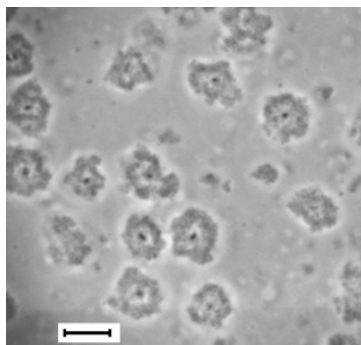


Fig.3 – Micrograph from a solution of tetra-block PEB-n copolymer in decane at 20°C; the scale bar represents 10 μm .



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Proposal number:	KW2-05-003, KW2-05-012, HAD-05-014		
Experiment title:	Investigating the GISANS method on KWS-2 – Part I and Part II		
Dates of experiment:	15.–20.04.2005 22.–28.06.2005	Date of report:	13.06.2006
Experimental team: Names	Addresses		
E. Kentzinger H. Frielinghaus U. Rücker Th. Brückel	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	H. Frielinghaus		

Experimental report text body

The aim of this experiment was to learn the Grazing Incidence SANS (GISANS) method. GISANS enables to study the in-plane correlations in a thin film sample on the 1-to-100 nm length scales. It is complementary to off-specular scattering at a reflectometer, method that probes the correlations in the 1-to-10 μm range.

GISANS can be performed at a SANS machine equipped with a precise goniometer at sample position. It uses the fact that, at a SANS machine, the beam impinges on the sample with a beam that is collimated along the two perpendicular directions perpendicular to the incoming wave vector $\mathbf{k}_i$. At a reflectometer, the beam is collimated only along one of those two directions and enables to resolve Q_x and Q_z as defined in Fig.1. At a SANS reflectometer, Q_y , the y-component of the scattering wave vector $\mathbf{Q}$, can also be resolved, allowing to probe correlations at the nanometer length scale (Fig. 1).

We show here some of the results obtained on a remanent polarizing $m=2.5$ supermirror. A study of its remagnetization process had already been performed on HADAS (c.f. report HAD-03-009). The aim was to obtain more information of the interface roughness and magnetic lateral correlations. We therefore measured the GISANS signal on this sample, varying the angle of incidence of the neutrons from 0 to 2.5° ($\lambda = 6.3 \text{ \AA}$), and at several applied magnetic fields. Also, several sample-wrt-beam geometries and several collimation and sample-to-detector distances have been probed.

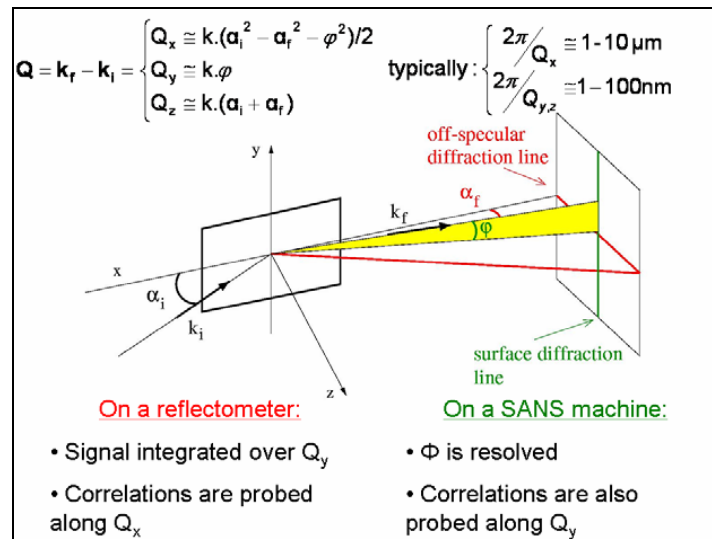


Fig.1: The GISANS geometry. Along Q_y , in-plane correlations can be probed in the 1-to-100 nm length scales.

We show in Fig.2 some of the results obtained with the applied field applied along the easy axis of magnetization and perpendicular to $\mathbf{k}_i$. Those data will be explained in the light of the polarized GISANS measurements presented in the report KW2-05-033.

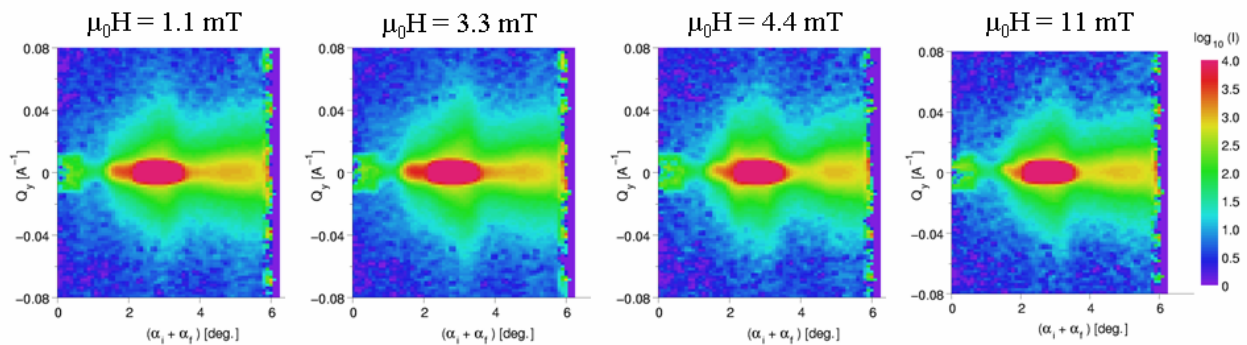


Fig.2: Field dependency of the GISANS signal measured on the supermirror at an angle of incidence $\alpha_i=1.5^\circ$, a collimation length of 8 m and a sample-to-detector distance of 3 m. Exposure time: 20 minutes per image.



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Proposal number:	KW2-05-004		
Experiment title:	Interactions of polymer and surfactant at the oil/water interface of monodisperse emulsions.		
Dates of experiment:	12.03. – 18.03.2006	Date of report:	30.06.2006
Experimental team: Names	Addresses		
Terence Cosgrove Dong Qiu Andrew Woodward	School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, U.K.		
Local Contact:	Jörg Stellbrink and Aurel Radulescu		

Experimental report text body

Oil in water emulsions will coalesce unless stabilised by an emulsifier. The most commonly used stabilisers are amphiphilic species such as surfactants and polymers. These chemical species reduce the interfacial tension between the oil and water phases. This is achieved by combining hydrophilic and hydrophobic moieties on one molecule. The molecules adsorb to the boundary between hydrophilic and hydrophobic phases, with the two moieties adsorbed into respective, favoured, phases.

Complex emulsion systems might contain more than one surface active species, in which case there will be competition for adsorption to the interface, and the formation of mixed micelles in solution. Our initial aim was to investigate the interaction between polymers and surfactants in emulsion systems.

We have formed monodisperse emulsions of poly-(dimethylsiloxane) in water. The emulsion were made using micro-fluidic chips that were designed based on those reported by Anna¹ and Xu². Using monodisperse emulsions reduces the need for statistical particle size distribution functions when fitting models to the scattering data.

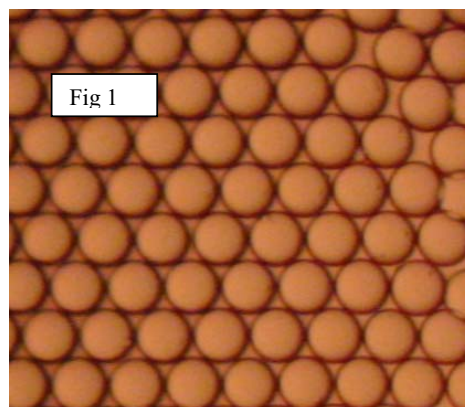


Figure 1 shows a monodisperse emulsion made from 50% deuterated PDMS [14K] and 50% hydrogenated PDMS [1K] with a size of approximately 40µm stabilized by H-SDS. This sample was contrast matched with a 44% D₂O 56% H₂O mixture. Unfortunately the samples were in very limited supply because of problems with the micro-fluidic device making it impossible to carry out the full range of experiments proposed.

Figure 2 shows a combined data set obtained from KWS-2 and KWS-3 for a sample of the PDMS emulsion in pure D₂O. There is a characteristic Q^{-4} decay from the emulsion/solution interface and the intensity at low Q is directly related to the surface/volume ratio in the sample. The minimum Q is $4.5 \times 10^{-5} \text{ \AA}^{-1}$ which sets a minimum size of approx 15 μm putting it outside of the range required for estimating the droplet size. It was our aim to make a smaller particle and to use data from DKD, but that data was unusable.

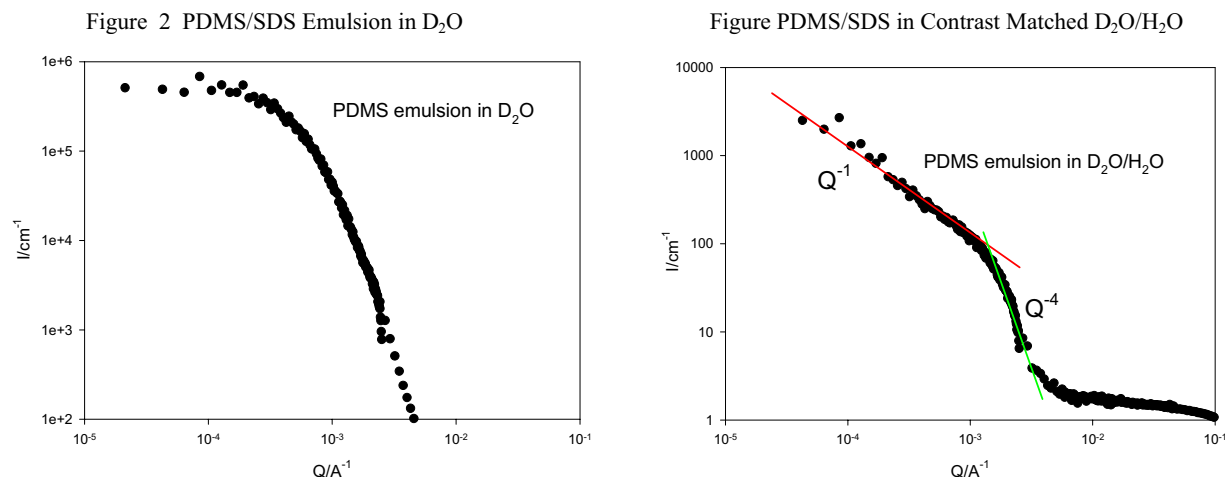


Figure 3 shows data with the emulsion contrast matched to a mixture of D₂O/H₂O. Under these circumstances the scattering from the emulsion is minimized. Unfortunately it proved impossible to make a pure D emulsion because of the high viscosity of the polymers available and a mixture of a high molecular weight D and a low molecular H were used. This meant that even under contrast match conditions there is some residual polymer scattering. The signal we were looking for was from H-SDS at the interface and it proved impossible to deconvolute these data. On a qualitative view the scattering showed three domains. At low Q a Q^{-1} which we believe originated from the polymer mixture. The Q^{-4} region may be a result of the emulsion not being fully contrasted. The high Q region may be attributable to the H-SDS.



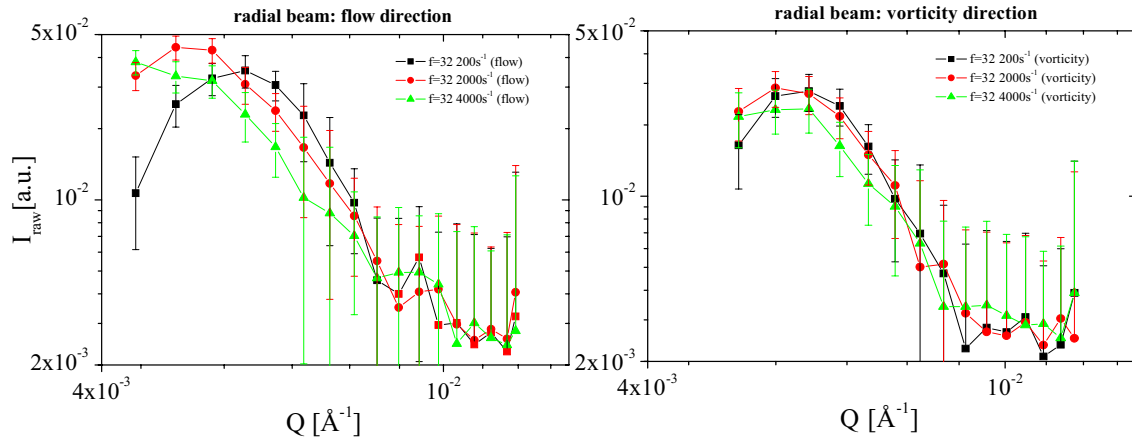
Experimental Report
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Proposal number:	KW2-05-005, KW2-06-007		
Experiment title:	Shear-induced deformation of low functionally star polymers		
Dates of experiment:	28.11.-30. 11. 2005 10.04.-13. 04. 2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink G. Rother B. Lonetti	IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

Ultra-soft colloids possess a soft shell and a hard core. They can be synthesized by, e.g., grafting flexible polymers to the surface of a sphere or by using block-copolymer micelles. The interesting feature of such systems is the possibility of a deformation of the soft shell in shear flow. In a recent theoretical work the structural and dynamical properties of ultra-soft colloids in shear flow was investigated [1]. The underlying model was based on a regular star polymer, i.e. f linear polymer chains with equal molecular weight M_w , tethered to a central microscopic core (the limiting ultra-soft colloids). Arm number f , arm length M_w , and shear rate $\dot{\gamma}$ was systematically varied. A strong deformation of the colloids in shear flow was observed. With increasing shear rate, the component of the radius-of-gyration tensor in the flow direction increases, whereas the other two components decrease. Thus, soft colloids with a larger number of arms are aligned to a less extent than those with a smaller number of arms. We expect that a system with a very large number of arms behaves essentially like a spherical object. Increasing the length of an arm from 10 monomers to 20 monomers yields a comparable behaviour. The slope of the curves is identical, merely the time scale is shifted, which corresponds to a different characteristic relaxation time. However, a crucial point in comparing theory with experiment for shear deformation of polymeric systems is the necessary minimum shear rate $\dot{\gamma}_{\min}$ to observe such a deformation. If the characteristic time of the experimental system, τ_c , is smaller than the inverse minimum shear rate, the system relaxes before any shear deformation can be observed. Recently it was found, that $\dot{\gamma}_{\min}$ seems to scale with N^{-2} , where N is the degree of polymerization (number of repeat units). Therefore high molecular weight polymers would be the ideal experimental system for such a comparison.

In our first experiment we investigated therefore high molecular weight poly(butadiene) star polymers [2] with intermediate functionality $f=6$ and $f=32$ in d-cis-decalin by means of Rheo-SANS experiments in radial configuration. The preliminary results show some evidence for the theoretically expected effects of external shear, although the data statistics are rather poor, see fig 1. Whereas along the vorticity (= neutral) direction the intensity seems to be more or less independent of the applied shear rate, along the flow direction there is a systematic shift towards lower Q -values indicating some extension of the star polymer.



In our second experiment we investigated the same star polymers in a solvent of much higher viscosity, i.e. deuterated bis-(2-ethylhexyl)-phthalate (DOP). DOP has a nearly two orders of magnitude higher viscosity than the previously used d-cis-decalin ($\approx 68\text{cp}$ instead of 3cp), which enhances the expected effect. Unfortunately it was not possible to keep the star polymers long enough dissolved to perform high quality SANS experiments. DOP is a marginal solvent for butadiene, so we had to compete with (partial) phase separation of the polymer, which crucially obstructs our experiment. Therefore we investigated in addition an 18-arm polyisoprene star polymer in DOP, which has a much lower $M_w=7500\text{g/mol}$, but here no effects of shear were observed.

References:

- [1] M. Ripoll, R. G. Winkler, and G. Gompper, *Phys. Rev. Letters*, **96**, 188302, 2006.
- [2] Stellbrink, J. Allgaier, D. Richter, A. Moussaid, A.B. Schofield, W.C.K. Poon, P.N. Pusey, P. Lindner, J. Dzubiella, C.N. Likos, H. Löwen, *Appl. Phys. A*, **74** [Suppl.], S355–S357, 2002.

f	$M_w \cdot 10^{-6} [\text{g/mol}]$	$D_{p,\text{arm}}$	$R_g [\text{\AA}]$	$B_w [\text{g/mol}]$	$A_2 \cdot 10^4 [\text{cm}^3 \text{mol/g}^2]$
2	0.57 ± 0.04	14685	510 ± 35	19.9 ± 0.4	9.60 ± 1.0
6	1.51 ± 0.06	5093	521 ± 6	19.9 ± 0.5	7.00 ± 0.24
16	3.45 ± 0.27	3537	511 ± 5	25.0 ± 1.2	2.96 ± 0.33
32	4.87 ± 0.39	2944	514 ± 5	22.0 ± 1.6	1.06 ± 0.28

Table 1: Molecular characteristics of the used poly(butadiene) star polymers obtained by SANS in perdeuterated cis-decaline [2]. M_w : molecular weight, $D_{p,\text{arm}}$: arm degree of polymerization, R_g : radius of gyration, B_w : blob molecular weight, A_2 : Second virial coefficient.

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Proposal number:	KW2-05-006		
Experiment title:	Investigating lateral magnetization correlations in exchange biased IrMn/CoFe multilayers		
Dates of experiment:	15.04.05	Date of report:	May 17, 2006
Experimental team: Names:	Amitesh Paul, Emmanuel Kentzinger, Henrich Frielinghaus, Thomas Brueckel		
Address:	Institut für Festkörperforschung Forschungszentrum Jülich GmbH D-52425 Jülich, Germany Deutschland		
Local contact:	Henrich Frielinghaus		

When a ferromagnet (FM)/antiferromagnetic (AF) bilayer is cooled below its blocking temperature in an external, a direct exchange coupling between FM and AF layers results in the shift of the hysteresis loop of the ferromagnetic layer (shift of the center from the zero field) along field axis which is termed as the exchange bias. Consequently, the hysteresis loop of the FM layer is usually shifted to negative fields.

The exchanged bias spin-valves studied in the present work are multilayer (ML) structures of $[Ir_{20}Mn_{80}(6.0nm)/Co_{80}Fe_{20}(3.0nm)] \times N$ prepared by dc magnetron sputtering, where N is the number of bilayers. The microstructure reveal a structural evolution of cluster sizes and shrinking of FM domains with N [1]. We found sequential switching of the layers that we relate to the microstructural evolution along the stack and no indication of coherent rotation of the magnetization was observed in our ML.

SF intensity maps for the specimen with N=10, when measured at HADAS show lateral magnetization fluctuations perpendicular to the applied field direction during the magnetization reversal. However, the length scales were much lower (200 Nm) than lateral coherence length of the neutron beam. A quantitative evaluation of the lateral length scale was beyond the scope of the present measurement geometry at HADAS. Thus in this work, therefore, we intended to measure the depth resolved length scales of such fluctuations perpendicular to the field direction which are originated from domains within the layers for the N=10 ML. We think GISANS technique is the unique way to explore such magnetization fluctuations which are directly linked to the magnetization reversal of exchange biased systems from vertically un-correlated magnetic domains.

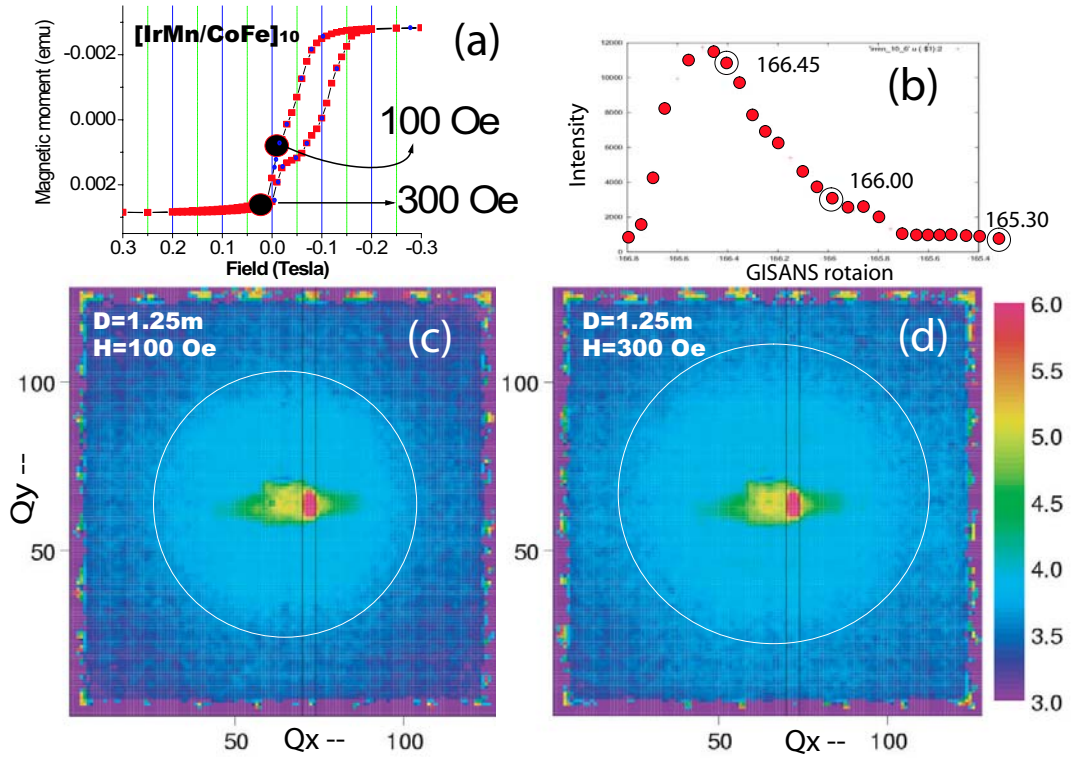


Figure 1. (a) SQUID hysteresis loop for $[\text{Ir}_{20}\text{Mn}_{80}(6.0\text{ nm})/\text{Co}_{80}\text{Fe}_{20}(3.0\text{ nm})]_{10}$ ML (b) GISANS rotating motor position indicating the measurement angle corresponding to the critical angle θ_c and other higher angles. (c) GISANS diffuse scattering spectra for two different applied fields (H) at a fixed D.

The measurements are done at two remanence fields for increasing [300 Oe] (Fig 1 (a)) and decreasing [100 Oe] fields with respect to the field cooling direction after saturating the specimen with + and - fields. We first determine the angles at which measurements are to be done. A specular scan of the intensity with increasing GISANS motor position give us the angles corresponding to three different regimes (Fig 1 (b)). In Fig 1 (c) and (d) are shown the intensity map for two different applied fields (H) at a fixed detector distance (D). Unfortunately, we can see only a halo of diffuse intensity around the specular beam (indicated in circle). These intensities at 100 Oe seems to grow to some extent at 300 Oe. This indicates, at least, the different size of the domains for the two remanence state of magnetization due to two opposite field history the sample undergoes. These diffusely scattered intensities are therefore supposedly arising from the domains within the layers of the ML stack. However, we could not observe the depth dependencies as expected even on varying with three detector distances. We find a possible problem in magnetizing the sample properly as there was no magnet available at the sample space which can induce a strong field of around 4.0 kOe to saturate the sample completely. The present results are nevertheless useful feedback for future measurements.

References

- [1] A. Paul *et al.*, Journ. Magn. Magn. Mater. **268**, 216, (2005); Phys. Rev. B **70**, 224410 (2004).



Experimental Report
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at the FRJ-2 Reactor

Proposal number:	KW2-05-007		
Experiment title:	CRITICAL FLUCTUATIONS AND ADSORPTION OF INDIVIDUAL FLUIDS CONFINED IN POROUS MEDIA: CONTINUATION		
Dates of experiment:	May 19. – May. 23, 2005	Date of report:	12-21-2005
Experimental team: Names	Addresses		
Y. B. Melnichenko G. D. Wignall D. R. Cole	Condensed Matter Sciences Division ORNL P.O.Box 2008 Oak Ridge, TN 37831-6393		
Local Contact:	Dr. H. Frielinghaus		

Experimental report text body

The adsorption of supercritical fluids in porous materials has been the subject of intense experimental and theoretical interest over the last decade. A supercritical fluid (SCF) is a substance at a pressure and temperature above its liquid-gas critical point where the coexisting (subcritical) liquid and gaseous phases become indistinguishable. At high pressure, the density of a SCF may become sufficient to provide substantial solvent power. At the same time, the diffusivity of solutes in SCFs is higher than in liquids due to a much lower viscosity, which facilitates mass transfer. The combination of tunable solvent power, practically unlimited miscibility with gases as well as advantageous mass transfer properties make SCFs an attractive alternative to subcritical (liquid) solvents for a variety of technological applications such as heterogeneous catalysis, adsorptive separations, regeneration of adsorbents and SCF chromatography [1]. Simplified theoretical considerations of heterogeneous processes are often based on an assumption that supercritical solvents in porous media can be treated as a continuum and thus the adsorption of the solvent molecules by the surface of solid porous adsorbents can be ignored. It is now being recognized however that when an adsorbate gas or supercritical fluid is in contact with a solid adsorbent, the attractive molecule-solid forces enhanced by strong micropore field effects can create a region near solid surface where the local adsorbate density is different from that in the homogeneous bulk phase [2]. The adsorbed phase is believed to extend to a distance of few molecular diameters from the surface far away from the critical point, and to become long ranged as the critical point is approached. An understanding of the structure and thermodynamic properties of the adsorbed phase at different conditions is fundamental to the successful development and optimization of reaction and separation processes involving SCF – solid interactions as well as to the fluid storage and carbon dioxide sequestration technologies [2].

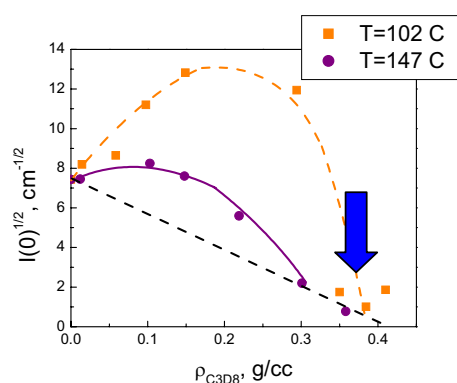


Fig.1. Variation of $I(0)$ of d-propane in aerogel at two different temperatures shown in the inset. ZAC for this system is reached at $\rho_{C3D8}=0.375$ g/cc (shown by the arrow).

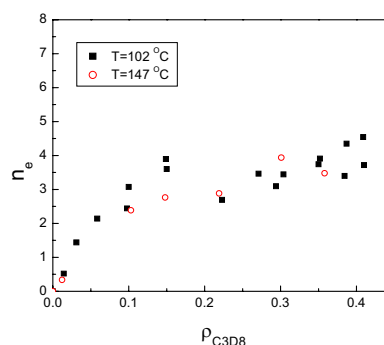


Fig.2. Variation of excess adsorption parameter for d-propane saturated aerogel with the fluid density at two temperatures shown in the inset.

During our recent experiments we were studying the adsorption behavior of deuterated propane in aerogels with the physical density of silica 0.1 g/cc which corresponds to the porosity of 96%. The aim of experiments was to compare the adsorption behavior of d-propane with that of supercritical carbon dioxide (SC CO₂) studied before at similar conditions [2]. From the point of view of SANS, the experimental condition for the two fluids in aerogel are very different as the zero average condition (ZAC) can not be reached for SC CO₂ which would require pressurizing the fluid to experimentally unachievable density of 1.27 g/cc [2]. At the same time, ZAC for d-propane in aerogel can be reached at $\rho_{C3D8}=0.375$ g/cc which lies within experimental window of the ORNL high pressure cell (see Fig. 1). This fact opens an interesting opportunity of extracting direct information about the density of adsorbed phase at ZAC condition.

Fig.2 shows the variation of excess adsorption of confined d-propane determined using a methodology described in [2]. The values of this parameter are an order of magnitude higher than excess adsorption of SCF in zeolites and superactivated carbons, although it is somewhat smaller than excess adsorption of CO₂ in similar aerogels. Another interesting difference between adsorption behavior of SC CO₂ and SC d-propane is the temperature invariance of excess adsorption of d-propane which indicates that the pores of the matrix are get filled with the adsorbed fluid already at temperatures exceeding the liquid-gas critical temperature ($T_c=97$ °C) by 50 degrees. The data processing of the pressure dependence of adsorption of d-propane in aerogels is now finished and a paper describing these effects is being written and will be submitted to JCP within few months. We hope to explore the variation of adsorption of d-propane with temperature during our next experimental session in February 2005.

- 1 Supercritical Fluids: Fundamentals for Applications (E. Kiran and J. M. H. Levelt-Sengers, eds), Kluwer Academic Publ., Dodrecht, Boston, London, 1993
- 2 Y. B. Melnichenko, G.D. Wignall, D. R. Cole, H. Frielinghaus, submitted to J. Chem. Phys.

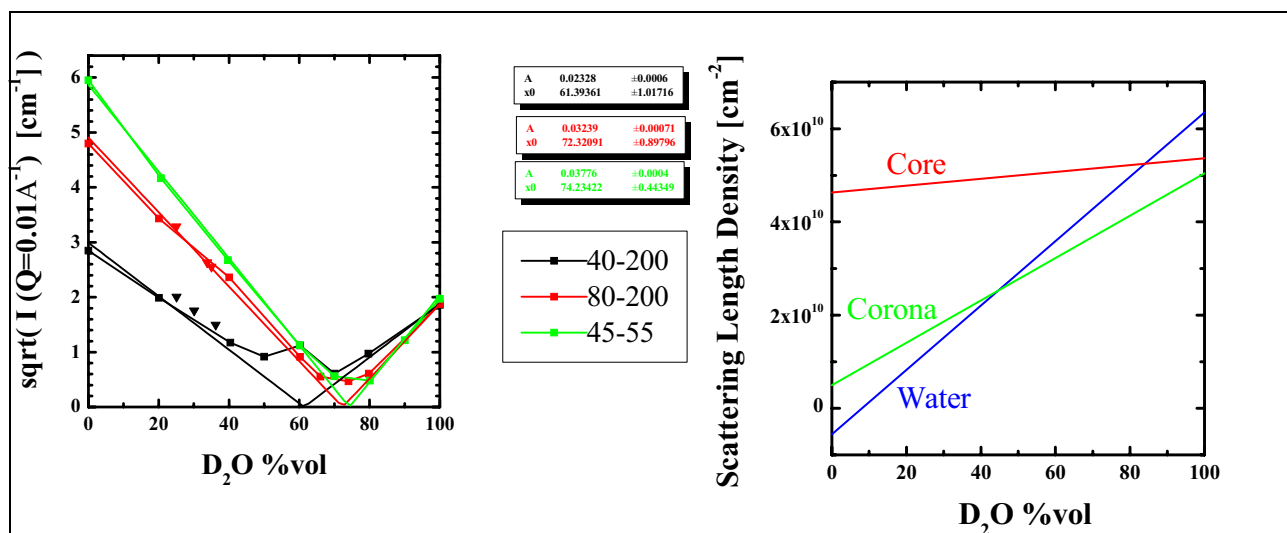


Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

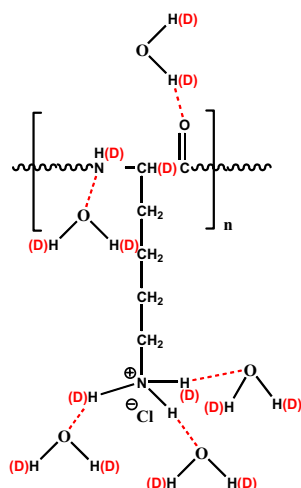
Proposal number:	KW2-05-008, KW2-05-042		
Experiment title:	Examination of the micellar behaviour of amphiphilic triblock copolypeptides of the ABA type, where A is polylysine and B is poly(γ -benzyl-L-glutamate), in water by SANS		
Dates of experiment:	25.08.05-06.09.05 and 16.01.06-23.01.06	Date of report:	25.05.06
Experimental team: Names	Addresses		
Hermis Iatrou Henrich Frielinghaus	University of Athens, Chemistry Department Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Germany		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

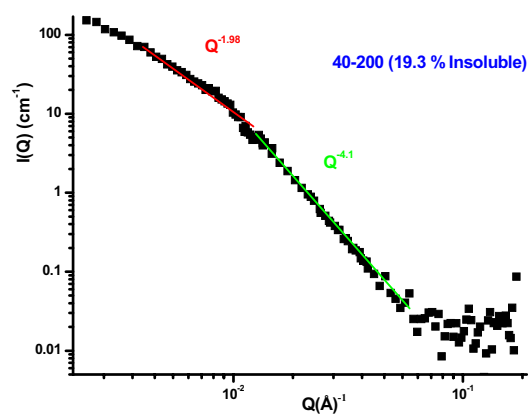
We have synthesized amphiphilic triblock copolypeptides of the ABA type, where A and B are poly-L-lysine and poly(γ -benzyl-L-glutamate), respectively. These copolypeptides are potential candidates for the formation of vesicles in water and conditions close to the one of the human body, very interesting for biomedical applications such as drug delivery systems. The synthesized triblock copolypeptides poly(-L-lysine)-b-poly(γ -benzyl-L-glutamate)-b-poly(-L-lysine) are amphiphilic copolypeptides, since the outer blocks are water soluble, whereas the middle block is insoluble. In order to distinguish where the insoluble and the soluble part exists within the aggregate, partially deuterated samples were synthesized, i.e. the benzyl groups of the poly(γ -benzyl-L-glutamate) part was partially deuterated. This gives enough contrast to match exactly either the core or the corona of the micelles that will be formed. Three different triblock copolypeptides have been synthesized, with the same molecular weights but different compositions, the 40-200, 80-200 and 45-55. The investigation of the micellar behaviour of amphiphilic triblock copolypeptides was performed in this project in a pH 7-8, at room temperature. Initial experiments were performed by LALLS in the University of Athens, which showed that the formed aggregates were large (about 100 nm radius) and spherical in shape. SANS was performed in KWS2, in order to find the molecular characteristics of the aggregates. First, we performed measurements of dilute solutions of the copolypeptides in mixtures of D₂O and H₂O, in order to calculate the scattering length density and the density of each part, i.e. the polylysine and PBLG parts. Then, measurements were performed in protonated and deuterated water in different concentrations. The contrast variation experiments gave a density of 1.13 g/ml for the polylysine part, and 1.32 for the PBLG part. Moreover, hydrogen bonding was assumed for the water soluble part of polylysine, where 5 molecules of water were linked to the polylysine molecule. Moreover, it was concluded that two of the hydrogens on the backbone of the aminoacids were exchanging with deuteriums, in order to match the experimental results (Scheme 2). The Scheme 1 shows the contrast variation experimental and fitted data.



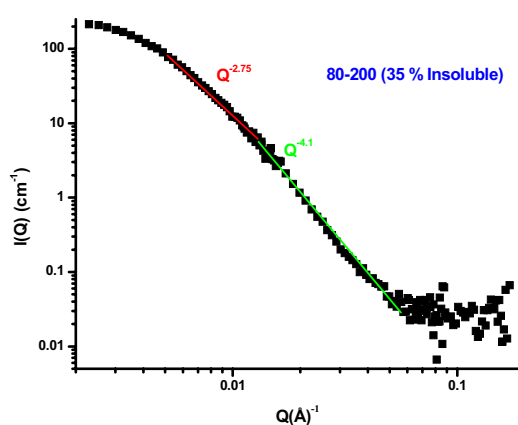
Scheme 1: Contrast Variation Experiments



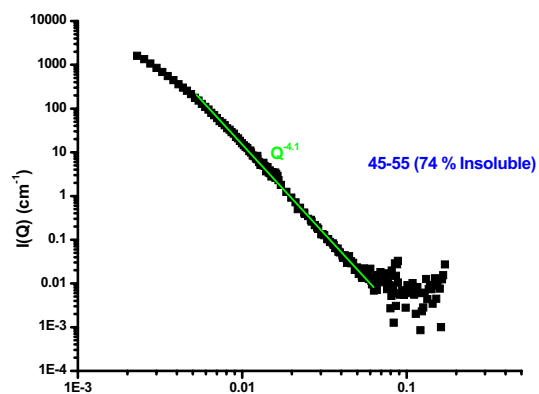
Scheme 2: Proposed form of the polylysine part



Scheme 3: $I(Q)=f(Q)$ for the 40-200 sample



Scheme 4: $I(Q)=f(Q)$ for the 80-200 sample



Scheme 5: $I(Q)=f(Q)$ for the 45-55 sample



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-009		
Experiment title:	Quantitative relationship between non linear mechanical properties and particle arrangement in model filled elastomers.		
Dates of experiment:	May 2005	Date of report:	March 2006
Experimental team: Names	Addresses		
Thomas Chaussée Hélène Montes	PPMD-ESPCI Esc H 10, rue Vauquelin 75005 PARIS		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Filled elastomers are widely used for their interesting mechanical properties that can be adapted to the use. But we do not understand how the surface interaction between the particle surface and the elastomeric matrix influences the mechanical behavior of so-filled elastomer. Therefore we decided to produce some model silica-filled elastomers using different grafts in order to modulate the surface interaction. Grafts studied are: n-Octyltriethoxysilane (C_8TES) and Hexamethydisilazane (HMDS) in order to perform a weak interaction and Acetoxyethyldimethylchlorosilane (MCSNC) to perform some hydrogen bonding.

The samples were prepared using the method using dialysis to get the silica suspension in the ethyl acrylate monomer. Suspensions were then adjusted to the right concentration by diluting the initially concentrated suspension, and a polymerizing initiator as well as a cross linker is added and polymerization is performed by alternative UV lighting. Before and during the polymerization step suspensions were cooled down to or $0^\circ C$ in order to freeze the system, or heated to $50^\circ C$ or $60^\circ C$ in order to bring some energy to deaggregate the particles during polymerization. The so obtained elastomers are then characterized by SANS in order to identify the dispersion state of the particle in the poly(ethyl acrylate) matrix.

Figure 1 didn't exhibit any correlation peak around $0.01 \text{ \AA}^{-1}$ q values, this means that there is no particular distance between two silica particles size. However it doesn't exhibit a strong increase in the low q region, it means that there shouldn't be any aggregates in the filled elastomers.

On figure 2 and 3 we are not able to see any difference on the Intensity curves whatever the size or the graft. It means that temperature has no influence on the dispersion state of the grafted silica particles.

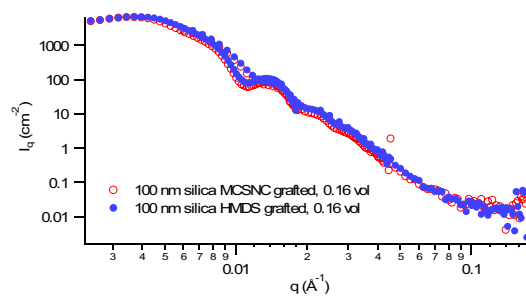


Fig. 1: 100 nm silica grafted HMDS or MCSNC synthesised at Room temperature

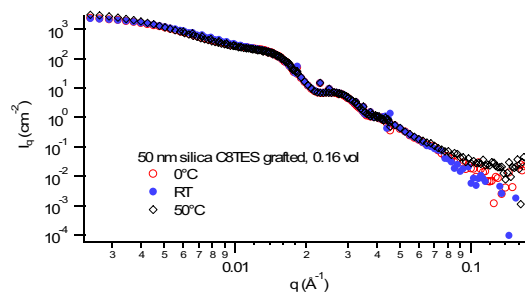


Fig. 2: 50 nm silica grafted C8TES synthesised at 0°C (red), RT (blue), 50°C (black)

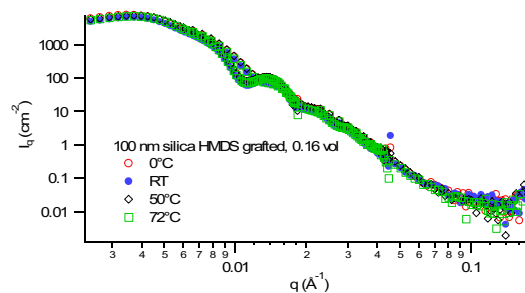


Fig. 3: 100 nm silica grafted HMDS synthesised at 0°C (red), RT (blue), 50°C (black) and 72°C (green)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-010, KW2-05-018, KW2-05-035		
Experiment title:	Confinement effects of diblock copolymers in bicontinuous microemulsions – part I, II, III		
Dates of experiment:	16. – 17.05. 2005, 24. – 26.08. 2005, 25. – 26.10. 2005	Date of report:	21.03.2006
Experimental team: Names	Addresses		
Simona Maccarrone Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Amphiphilic diblock copolymers have approved to increase the efficiency of surfactants dramatically (polymer boosting effect). In the first studies [1] the domain size of oil or water domains was relatively large compared to the polymer size. Initial simulations by Auth [2] predicted deviations from the ideal behaviour with increasing confinement of the polymer. At intermediate confinement the efficiency boosting is even more dramatic. At high confinement a reversed behaviour is predicted. The current study investigates the sensitivity of the polymer boosting effect as a function of the degree of confinement.

Microemulsions consist of immiscible oil and water. The third component, the surfactant, mediates between oil and water. Domains of pure oil and water are formed, whose surfaces are covered by the amphiphile. For equal volumes of oil and water a minimum amount of surfactant is needed to form a one-phase bicontinuous microemulsion. This amount is a measure for the efficiency of the surfactant.

When adding amphiphilic diblock copolymers to the microemulsion, this macro surfactant molecule is anchored in the surfactant membrane, and the two different blocks are situated in their pleasant environment [1]. Furthermore, it was shown that the diblock copolymer increases the bending rigidity. This result explains the empirically found polymer boosting effect, which describes a drastic enhancement of the surfactant efficiency. Stiffer membranes allow the formation of larger domains with a better surface to volume ratio. Theories agree well with these first studies.

Several bicontinuous microemulsions were studied intensively in phase diagram measurements. A single relatively large diblock copolymer PEP₂₂-PEO₂₂ was chosen. The domain spacing of the microemulsions was varied by the use of different oils (hexane, octane, decane, undecane, dodecane, tridecane, tetradecane) influencing the efficiency primarily. The polymer amount over the total amphiphile quantity that we could add changes significantly going from the shortest chain oils (4 %) up to the longest chain oils (0.025%) leaving the phase diagrams almost unchanged.

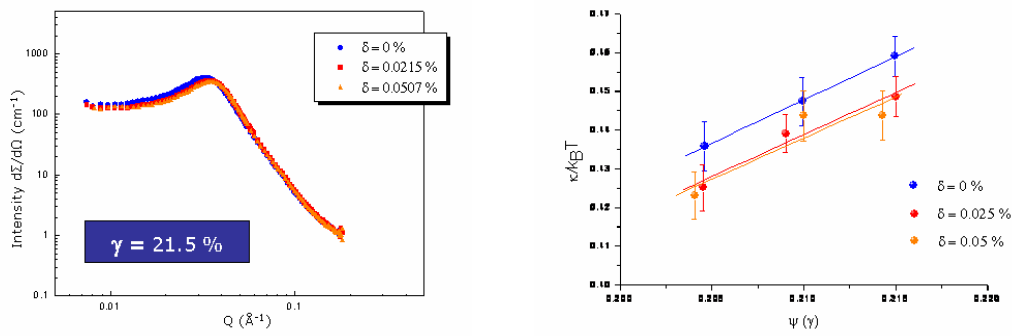


Figure 1. The plot on the left shows how, at fixed concentration, the addition of polymer doesn't affect visibly the peak width for tetradecane microemulsions. On the right, we have the decreasing of the bending rigidity κ as far as we add some polymer.

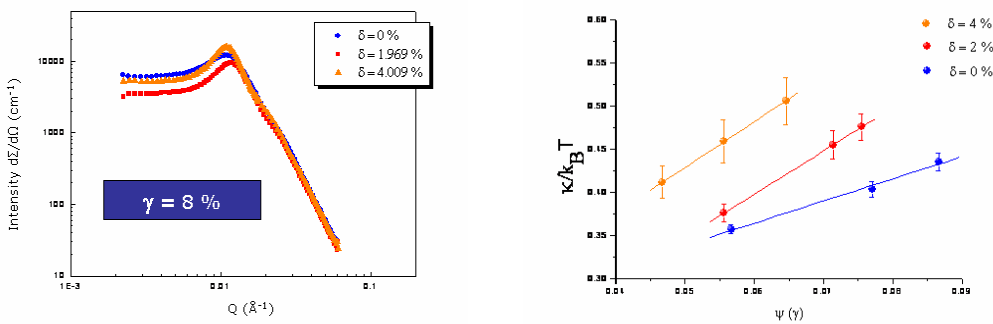


Figure 2. The plot on the left shows how, at fixed concentration, the addition of polymer for hexane systems can affect the peak width. On the right, we have the increasing of the bending rigidity κ with polymer addition.

By small angle neutron scattering (SANS) the structure of a microemulsion is studied, which can be characterized by the domain spacing d and the correlation length ξ . The Gaussian random field theory connects these two parameters with the bending rigidity κ .

As examples, we can see the behaviour of the 2 extreme cases: tetradecane and hexane systems. For the former, it seems to not have significant variations of the peak position as well as the width (fig.1 left). But performing the calculations of the bending rigidity we found a decreasing of κ with polymer addition (fig.1 right "antiboosting effect").

For the latter, it was found the reverse behaviour. As it is shown in the fig.2, the peak is affected by the polymer presence on the membrane, and becomes sharper that means an increasing of the correlations length. In this case, the bending rigidity increases because we have more polymer on the membrane surface, that becomes more rigid.

After collecting all these data, we are also able to draw the sensitivity rate Ξ of the variation of κ as a function of confinement expresses by the inverse of the ratio d/R_g where d is the domain size and R_g is the radius of gyration of our polymer. To cover a wider range of confinement we measured subsequently also hexane, eptane, octane and decane using a smaller polymer PEO₁₀-PEO₁₀ in order to get more points in delimitation of the curve. What we observed is a constant value of Ξ for the low confinement regime (more efficient microemulsions with short chain oils) that means that polymer is comfortable in the domains but with a lot of space that doesn't allow it to affect so much the membrane stiffness. Then the intermediate regime comes with a slight increasing around $d/R_g \sim 4$ and a strong decreasing after $d/R_g \sim 2$ for high confinement as a proof of the antibooster behaviour of the less efficient micromulsions with long chain oils. The whole measured behaviour agrees semi-quantitatively with the theoretical prediction (simulation by Auth [2]).

[1] B. Jakobs, T. Sottmann, R. Strey, J. Allgaier, L. Willner, D. Richter *Langmuir* **15**, 6707 (1999)

[2] PhD thesis: T. Auth, University Köln, 2003



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-011		
Experiment title:	Test measurements of Co nanoparticles in microemulsion		
Dates of experiment:	17.06 – 20.06.05	Date of report:	14.03.06
Experimental team: Names	Addresses		
Feygenson Mikhail, Pollmeier Klaus, Kentzinger Emmanuel Dr.,	Forschungszentrum Jülich GmbH Institut Für Festkörperforschung (IFF-STM) D-52425 Jülich Germany		
Sager Wiebke Dr.,	Forschungszentrum Jülich GmbH Institut Für Festkörperforschung (IFF-IWM) D-52425 Jülich Germany		
Local Contact:	Dr. Henrich Frielinghaus		

Experimental report text body

We have produced cobalt nanoparticles in a microemulsion following the recipe given by Pileni et. al., (1999). The microemulsion is of the so called water-in-oil type and consists of water droplets surrounded by surfactant molecules Igepal or $C_{12}E_5$. We used mixture of deuterated and protonated oil in order to reduce the incoherent scattering from hydrogen as well as to obtain different contrasts in the system. The particles obtained are small enough (typically 6 to 10 nm) to be mono-domain.

The aim was to measure the magnetic and the nuclear form factors of the cobalt nanoparticles, F_M and F_N , respectively and the structure factor in an external magnetic field.

The number of microemulsions containing Co nanoparticles were prepared and stabilized by both surfactants. We have found two appropriate contrasts for the samples. They contain such amount of protonated water and oil to have a reasonable level of the incoherent scattering. These are: “shell” contrast – when the scattering length density (SLD) of water matches the one for the oil and Co nanoparticles themselves. The second one is “core-shell” contrast with 100 % deuterated oil and water. The magnet with maximum field up to 0.4T and direction perpendicular to the incoming neutron beam was used.

The first measurements of Co nanoparticles in the “core-shell” contrast displayed the scattered intensity with two pronounced minima (Fig.1). The first minimum at $Q = 0.1 \text{ \AA}^{-1}$ was attributed to the scattering from water droplets and the second one at $Q = 0.18 \text{ \AA}^{-1}$ was recognized as the scattering from Co nanoparticles with sizes smaller than the size of the droplets. The scattering curve did not show any applied magnetic field dependence. Then the measurements of deuterated hexane (Fig.2.) were carried out. Unexpectedly, the minimum shows up at $Q = 0.18 \text{ \AA}^{-1}$. It turned out that at the detector distance $D = 1.25\text{m}$ the sample position was too far from the detector which leads to the artificial minimum at higher Q values. The problem was recognized and solved at the last day of the beam time. In Fig.2. the re-measured d-hexane with correct setup is shown.

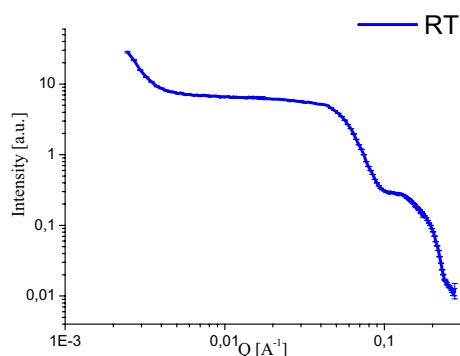


Fig.1. Co nanoparticles in microemulsion (core-shell contrast)

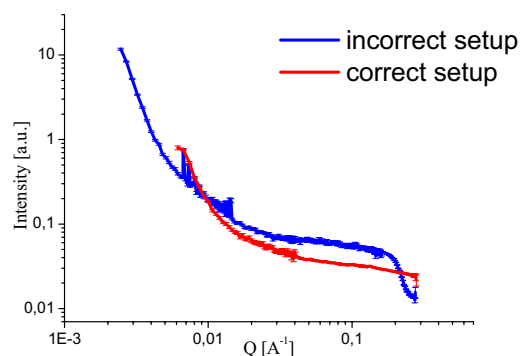


Fig.2. Scattering curve of d-hexane at two setups

From this figure we were able to distinguish between the real scattering from the sample and the artificial minimum at higher Q . Due to time constraints, the calibration measurements could not be done properly, which makes impossible to reduce the data to the absolute units.

Despite the technical problems the qualitative conclusions can be made.

Samples re-measured with correct setup did not show a minimum at higher Q which would characterize the Co nanoparticles. The scattering from the water droplets suppressed the scattering from the particles themselves due to the low content of cobalt in a microemulsion.

The next step will be to extract Co nanoparticles from microemulsions and re-disperse them into solution.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-013; KW2-05-022; KW3-05-002		
Experiment title:	Paraffin crystallization in solution in the presence of multi-segment PEB-n random copolymers (parts 1, 2 and 3)		
Dates of experiment:	08.06.05-16.06.05 28.11.05-01.12.05	Date of report:	29.05.06
Experimental team: Names	Addresses		
Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.H.Frielinghaus, Dr.E.Kentzinger		

Experimental report text body

The self-assembly of poly(co-olefins) in dilute solution has been shown via SANS to yield either plate-like or needle-like micelles-like micelles [1,2]. The resultant supramolecular structures are dependent upon the copolymer architecture. The crystalline-amorphous diblock co-polymers yield self-assembled hairy plates while the corresponding random co-polymers yield one-dimensional needle shaped aggregates. The PEB-n random copolymers (n - the number of ethyl sides per 100 backbone carbons) show selectivity in their wax crystal modification capacities depending on the ethylene content of the backbone. This behavior relates to the graded ethylene content of PEB-n copolymers that leads to different self-assembling temperatures: the lower n, the higher the self-assembling temperature [2]. All PEB-n copolymers self-assemble in open 1-d structures. This conclusion has stimulated further structural studies of multiblock copolymers in solution where blocks represent poly(ethylene-butene) random copolymers (PEB-n) showing graded ethylene contents and thus, different crystallization degrees. Recently [3] conventional and focusing SANS studies of self-assembling in decane solution of a triblock and tetrablock PEB-n copolymers have been performed. The structural results complimented by microscopy observations concluded that these materials form in solution core-shell structures showing a 1D overall aspect which associate and give raise to occurrence of large scale spherulitic-like soft aggregates with sizes within the micrometric range. In the present study we investigated the wax crystal modification capacity of the triblock and tetrablock PEB-n copolymers by performing conventional and focusing SANS experiments on different wax-copolymer mixtures in decane and for different wax concentrations. Mainly three wax-copolymer combinations have been studied over a wide temperature range, between the single coil temperature (typical at 85°C) and the common aggregation regime, well below 0°C: the triblock PEB-6.5/8.9/10.1 was combined with 1% and 4% C24 tetracosane and with 1% C36 hexatriacontane while the tetrablock PEB-2.6/6.0/10.9/13.2 copolymer was combined with 0.5%, 1%, and 4% C36 hexatriacontane. The study aimed at first the modification of the wax crystals structure under the polymer

influence comparing with the pure wax solutions in decane. The conventional SANS investigations have shown that both waxes form in decreasing temperature under the influence of these multiblock copolymers 2-dimensional thin aggregates and do not grow anymore into big compact crystals with sizes of hundred of micrometers as in the case of pure wax solution. Examples of the wax scattering patterns for two wax-multiblock copolymer mixtures are presented in Fig.1 and 2. The Q^{-2} power law behaviour is indicative for scattering from 2D aggregates while the thickness of such aggregates can be evaluated from the Guinier regime observed towards high Q . The inset of Fig.1 present a 2D Guinier plot of the scattering pattern which allows a direct evaluation of the aggregate thickness and concludes that the wax form monolayers whose thickness is given by the length of the wax molecules, about 32Å and 45Å in the case of C₂₄ and C₃₆ waxes, respectively. At low Q and for low temperature conditions the scattering patterns show an increasing intensity which deviates from the Q^{-2} power law and proves that the wax is involved in some large scale aggregates. From this observation and taking into account that the multiblock copolymers yield large spherulitic-like soft aggregates showing a strong scattering at very low Q (focusing SANS range) we may conclude that the wax platelets formed under the polymer influence template to some extent the polymer morphology and show an association or agglomeration which gives raise to occurrence of large scale waxy structures too. However, the microscopy observation have shown that the mixed aggregates of waxes and multiblock copolymers present almost the same morphology like those formed by the polymer alone and have even a slightly smaller size than these ones. The focusing SANS experiments performed on the same samples under the wax contrast conditions provided unreliable results as long as the samples transmission was very low. Because the multiblock copolymers have been available only in protonated state in order to match them with the solvent and to have only the wax “visible” for the SANS investigations protonated solvent was required. In this way at KWS3 multiple scattering effects dominated and led to unsatisfactory data.

References: [1] D.Schwahn et al., Macromolecules 35, 861, 2002; [2] A.Radulescu et al. J.Pol.Sci. B Pol.Phys. 42, 3113, 2004; [3] experimental reports KW2-05-002;KW3-05-001 FRJ-2 Jülich.

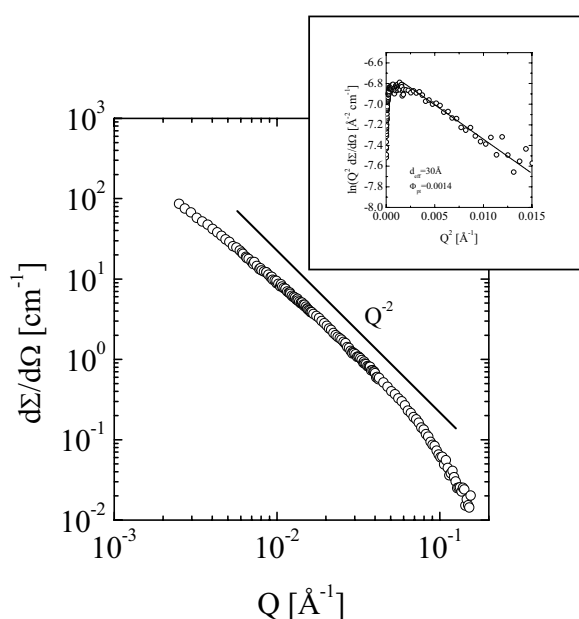


Fig.1 – The scattering pattern under the wax contrast form a mixture of 1% C24 and 1% triblock copolymer in decane at -20°C. The inset shows a 2D Guinier plot allowing the evaluation of the thickness of wax platelets.

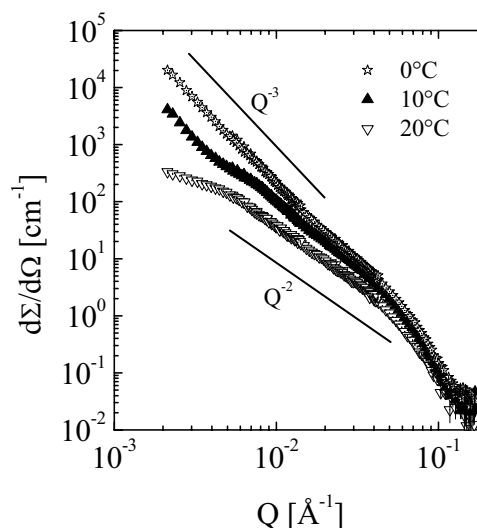


Fig.2 – The temperature evolution of the wax scattering pattern for a mixture of 1% C36 and 1% tetrablock copolymer in decane.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-014, KW3-05-005		
Experiment title:	T-induced jamming in dense solution of star-like micelles		
Dates of experiment:	23.5.-25. 5. 2005 19.4.-24. 4. 2005 24.8.-26. 8. 2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink G. Rother	IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

Recently we investigated the phase behaviour of star-like micelles formed by the amphiphilic block copolymer poly(ethylenepropylene)-poly(ethyleneoxide), $M_{w,PEP} = 1000$ g/mol, $M_{w,PEO} = 20000$ g/mol, in different water/DMF mixtures by small angle neutron scattering (SANS) [1] and partly by light scattering and rheology. Changing the solvent composition changes the aggregation number (or functionality) of the micelles due to changes in the interfacial tension between the core-forming, hydrophobic PEP and the solvent. This enabled us to construct the equilibrium phase diagram in the packing fraction (η) / functionality (f) representation and compare it to theoretical predictions for regular star polymers [2]. Still under discussion is the competition between vitrification and crystallization. For star-like micelles no crystal formation was observed at $f \geq 70$ as predicted by theory. Here an amorphous gel or glass phase was found above the overlap packing fraction η^* . At smaller functionalities, i.e. $f \leq 70$, on the other hand, the predicted bcc-structure was found experimentally. This is in contradiction to experimental observations for regular star polymer solutions, where for all f only amorphous phases were found.

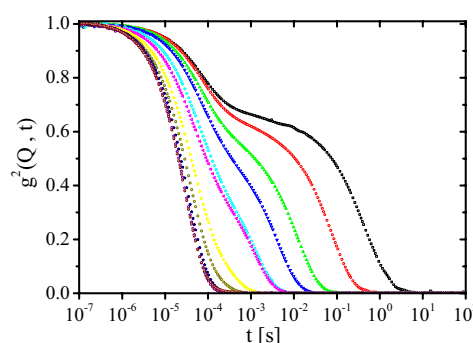


Figure 1: Intensity autocorrelation function $g^2(Q, t)$ observed in a dynamic light scattering experiment for a dense solution of star-like micelles, $\Phi = 3\%$, $T = 80^\circ\text{C} \rightarrow 4^\circ\text{C}$ (from left to right).

By dynamic light scattering we found experimental evidence for a temperature induced glass transition resulting from a change in packing fraction, which originates from a temperature induced change in solvent quality, see fig.1. This phenomenon is similar to what has recently been observed for regular star polymers by Kapnistos et al. [3].

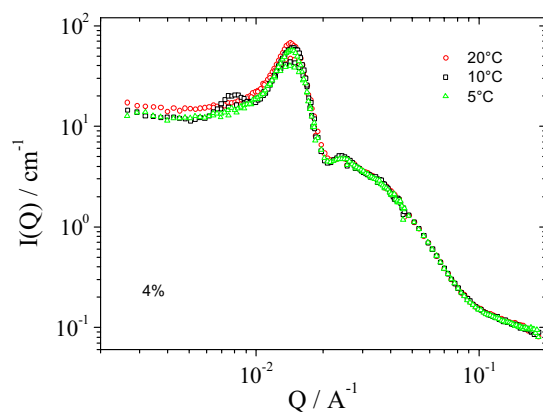


Figure 2: Temperature dependent SANS intensity for star-like PEP1-PEO20 micelles in D2O (full contrast), $\Phi=0.04$.

In this experiment we followed the T-induced changes in the static structure factor $S(Q)$ by small angle neutron scattering (SANS, KW1) and ultra-small angle neutron scattering (U-SANS, KW3) and observed some interesting changes in particular in the low-Q-regime, see fig. 2. Here the T-dependent occurrence of a pre-peak is clearly visible, which indicates some changes in the microscopic structure although macroscopically (rheology) the sample was found to be in the solid state for all temperatures shown. Liquid samples, on the other hand, just showed a T-dependent broadening of the main structure factor peak.

To extend the Q-range we also investigated some samples by U-SANS (KW3) to check for some T-induced clustering, but unfortunately the intensity of all samples was only slightly above the background,

so that no data with reasonable statistics could be collected.

In summary, all these results show that star-like PEP-PEO micelles are an easy-to-establish, “tuneable” model system for regular star polymers (ultra-soft colloids)..

References:

- [1] R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, *Macromolecules*, **37**, 9984, 2004.
- [2] M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, *Phys. Rev. Letters*, **94**, 195504, 2005.
- [3] M. Kapnistos *et al.*, *Phys. Rev. Lett.* **85**, 4072, 2000.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-015		
Experiment title:	Transition from droplets to bicontinuous structures via cylindrical networks: experiment as support for theory		
Dates of experiment:	15.08.2006-19.08.2006	Date of report:	18.05.2006
Experimental team: Names	Addresses:		
Tobias Foster Thomas Sottmann	Institute for Physical Chemistry, Luxemburger Str. 116, 50939 Cologne, Germany		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

One of the most difficult, fascinating and still unsolved problems in the fundamental research on microemulsion systems is the understanding of how a globular microemulsion (e.g. water droplets in a continuous oil phase) transforms into a disordered, bicontinuous structure. In the recent years theories were developed which predict this structural transition to occur via an intermediate, thermodynamically stable phase of cylinders that, near the bicontinuous region of the phase diagram, join up into a complex network structure [1].

The first evidence for this transition relies on experimental studies of microemulsion phase behaviour and viscosity, as well as on measurements of the electric conductivity of oil-rich microemulsions. Figure 1a shows a typical phase diagram for oil-rich microemulsions, here for the system $D_2O - n\text{-decane}(d22) - C_{10}E_4$. The microemulsion phase (1) is found for intermediate temperatures, with two-phase regions for higher- ($\bar{2}$) and lower (2) temperatures. Samples are characterized by surfactant/(oil+surfactant) mass fraction γ_b and the water mass fraction w_A . For nonionic water-in-oil microemulsions, the mentioned spherical or globular structures are found at temperatures just below of the *wefb* (Fig1a). As the temperature is decreased, the spontaneous curvature (negative by definition for w/o-droplets) of the amphiphilic film increases [2], and elongated, cylindrical structures are formed. These structures branch at temperatures sufficiently close to the lower phase boundary to form a system-spanning network of connected cylinders.

This transition from discrete- to connected structures can be monitored by measurements of the electric conductivity which increases by several orders of magnitude when the temperature is lowered starting from the *wefb*. This trend is shown in Figure 1b.) for an oil-rich microemulsion of the system $H_2O/NaCl - n\text{-decane}(h22) - C_{10}E_4$, whereby addition of NaCl (mass-fraction ϵ of $NaCl/(water+NaCl)$) assures sufficient conductivity of the water-phase.

This structural transition from globular- to bicontinuous microstructure can be monitored by systematic

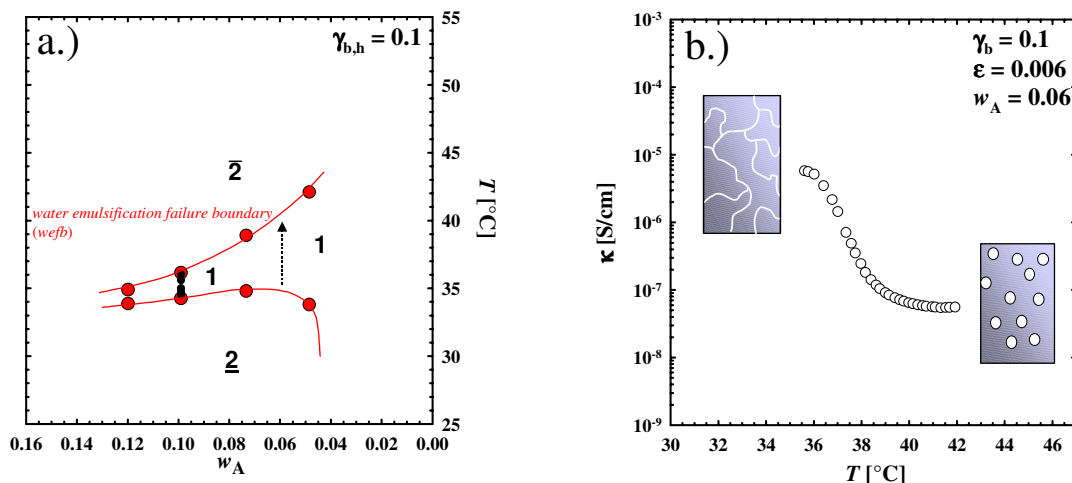


Figure 1: a.) Phase diagram of the oil-rich side in the system $D_2O - n\text{-decane}(d22) - C_{10}E_4$, with sample compositions characterized by the mass fractions γ_b and w_A (definitions and more details see text). b.) electric conductivity of a microemulsion sample in the system $H_2O/NaCl - n\text{-decane}(h22) - C_{10}E_4$ when the temperature is increased as indicated by the dotted arrow in a.).

temperature dependent neutron scattering measurements. The black points in Figure 1a.) indicate the temperatures studied for one given composition of the sample. Exemplary temperature dependent scattering curves are shown in Figure 2a.). With decreasing temperature, the forward scattering intensity

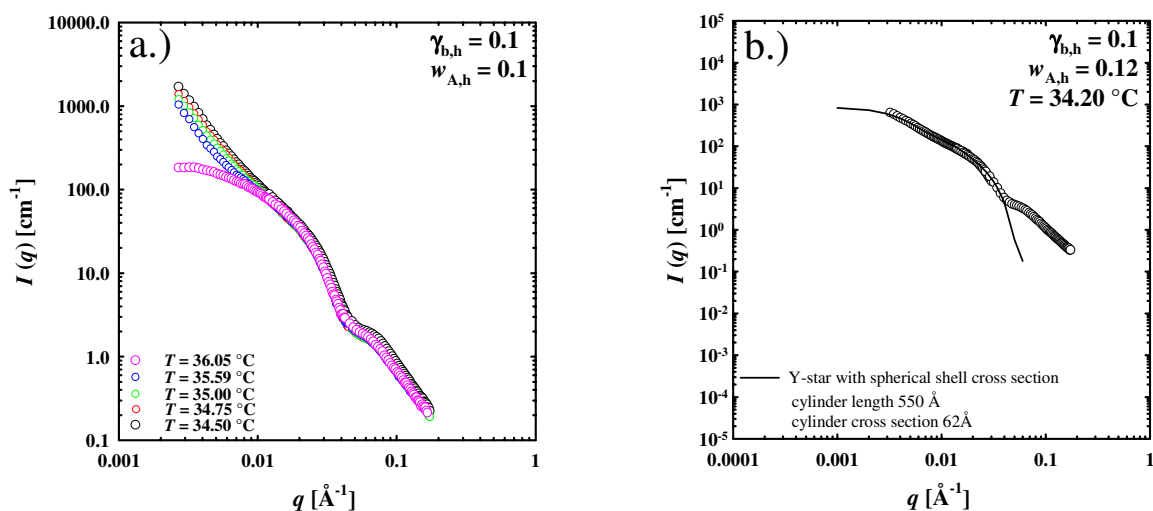


Figure 2: a.) Representative neutron scattering data for $D_2O - n\text{-decane}(d22) - C_{10}E_4$ microemulsions at various temperatures. b.) representative fit of the low-temperature SANS data with a model derived in collaboration with Sam Safran, Weizmann Institute of Science.

increases strongly, indicating the formation of large structures. Furthermore, the pronounced q^{-1} -decay for intermediate q -values indicates the presence of cylindrical structures. The data are currently analyzed using a novel form factor for the scattering from three long cylinders which are joined by network junctions. A typical result is shown in Figure 2b), yielding two length scales, namely the lengths of the cylinders and the radius of the cylinder cross section.

- [1] T. Tlusty et al., *Phys.Rev.Letts.* **78**, 2616 (1997).
- [2] R. Strey, *Colloid and Polymer Sci.* **272**, 1005 (1994).



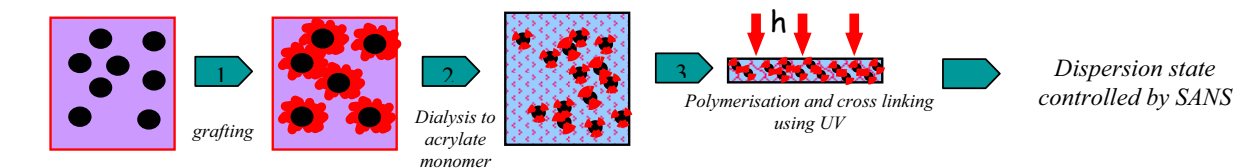
Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-016		
Experiment title:	Quantitative relationship between non linear mechanical properties and particle arrangement in model filled elastomers.		
Dates of experiment:	December 2005	Date of report:	March 2006
Experimental team: Names	Addresses		
Thomas Chaussée Hélène Montes	PPMD-ESPCI Esc H 10, rue Vauquelin 75005 PARIS		
Local Contact:	Henrich Frielinghaus		

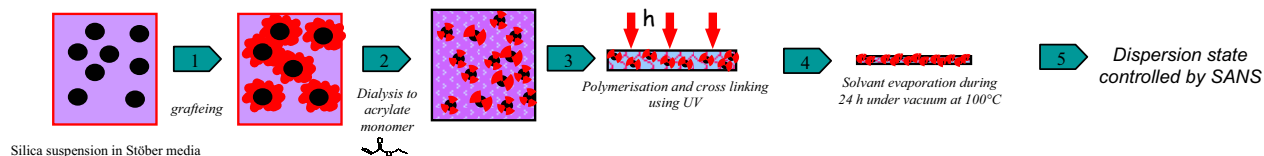
Experimental report text body

Filled elastomers are widely used for their interesting mechanical properties that can be adapt to the use. But we do not understand how the interactions between the particle surface and the elastomeric matrix influences the mechanical behavior of so-filled elastomers. Therefore we decided to produce some model silica-filled elastomers using different grafts in order to modulate the surface interaction. Grafts studied are: n-Octyltriethoxysilane (C8TES) and Hexamethyldisilazane (HMDS) in order to perform a weak interaction and Acetoxyethyltrimethylchlorosilane (MCSNC) to perform some hydrogen bonding.

In previous work we used Ford method to synthesize our elastomers. The protocol could be schematized as follow:



This leads for weak interaction to an aggregation of the particles while polymerizing the elastomer. Therefore we decided to modify the protocol as follow:



We think that the use of a co-solvent will help to avoid depletion phenomenon during the polymerization. Results (fig. 1 to 3) show that the addition of ethanol leads to better dispersion states whatever the silica concentration, size or the graft. For example in fig. 1 we observe for 100 nm C8TES-grafted silica systems (synthesised in the presence of ethanol 1/1, w/w) a correlation peak at $0.08 \text{ \AA}^{-1}$ whereas the synthesis without solvent leads to increase at low q characteristic of the presence of big particle aggregates.

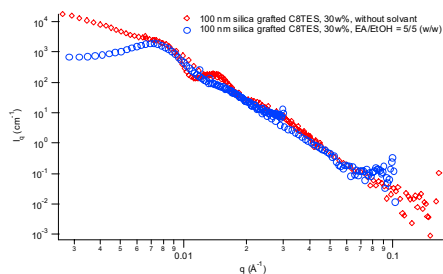


Fig. 2: 100 nm HC8TES-grafted silica, synthesised in the presence of ethanol (blue) or without any co-solvent (red)

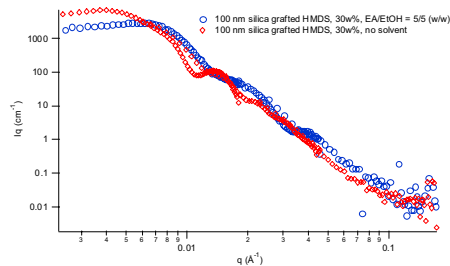


Fig. 2: 100 nm HMDS-grafted silica, synthesised in the presence of ethanol (blue) or without any co-solvent (red)

The presence of a co-solvent is the way to obtain well dispersed silica whatever the interaction between the matrix and the particle is.

We now need to work on the type of co-solvent used to improve the quality of the dispersion and to see in which condition (quantity of solvent, quantity of cross-linker and polymerization initiator) it is possible to obtain a polymer matrix having the required mechanical behavior.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-017		
Experiment title:	Self-assembly mechanism in octo-peptide gels		
Dates of experiment:	24.10. – 28.10.2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
A. Saiani A. Mohammed	School of Materials, The University of Manchester, Grosvenor Street, Manchester, M1 7HS, UK		
A. Miller A. Konstantopoulos R. Zhang	School of Chemical Engineering and Analytical Science, The University of Manchester, Sackville Street, Manchester, PO Box 88, M60 1QD, UK		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

We have investigated the self-assembling and gelation properties of a set of octa-peptides based on the following amino acids: alanine (A), phenylalanine (F), lysine (K; charge +), arginine (R charge +), glutamic acid (E; charge –) and aspartic acid (D; charge –). The amino acid sequence has been varied in order to create two types of octa-peptides one with alternating charges and one with charges located at the two end of the peptide. The overall peptide charge was kept neutral. The peptides investigated are summarized below:

AEAEAKAK	FEFEFKFK	FDFDFKFK	FDFDFRFR
AEAKAEAK	FEFKFEFK	FDFKFDFK	FDFRFDFR

Peptide solutions and gels were prepared by dissolving the desired amount of peptide in deuterated water at high temperature, 80°C. The solutions were then cooled at room temperature and depending on the peptide sequence and the overall concentration gels were formed.

Except for the alanine based peptides it was found that the scattering profiles of our samples did not depend on the sequencing but on the type of amino acid used in the sequence. Very different scattering patterns were obtained as illustrated in figure 1 for the different octa-peptides.

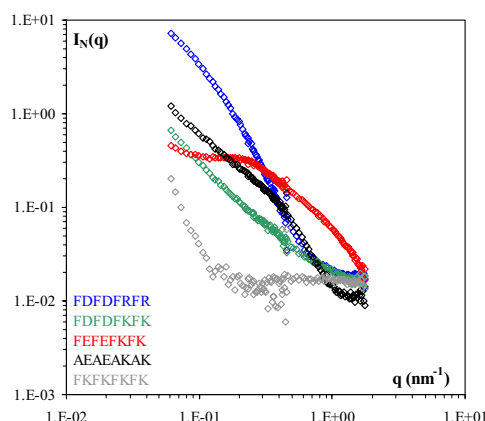


Figure 1: Intensity scattered by the different peptides samples (Conc. 20 mg ml⁻¹).

Figure 2 shows a Kratky plot ($q^2 I(q)$ vs. q) of the intensities scattered by the AEAEAKAK solutions at 10 and 80 mg ml⁻¹. As can be seen characteristic curves of rod-like structures were obtained. The data could be fitted using a plain-rod model as described by equation 1.

$$q^2 I_A = 4\pi q C_D \mu_L \left[\frac{J_1(qr)}{qr} \right]^2 \quad (1)$$

The agreement between the model and the experimental curves was found to be good. These results suggest that AEAEAKAK peptide does self-assemble and form rod-like structures i.e. fibers in solution. A diameter of ~ 6 nm was obtained for the fibers diameter for both samples. No gels were formed on cooling indicating that these fibers

are not able to aggregate or entangle and form 3D networks and hydrogels at the investigated concentrations. For the AEAKAEAK peptide the scattering patterns do not suggest the presence of any structure. This seems to indicate that this peptide does not self assemble in solution at the concentrations investigated underlining the important role played by the amino acid sequence

When alanine is replaced by phenylalanine gels are formed readily. The scattering curves for FEFEFKFK samples are shown in figure 3. A clear scattering maxima is observed in the $I(q)$ vs q curve when the samples form gels. The two lower concentrations 2 and 5 mg ml⁻¹ do not form gels. Using the Bragg relation ($d = 2\pi/q^*$) an estimation of the mesh size of the gel can be obtained from the position of the maxima. In our case depending on the concentration 15 to 30 nm is obtained for the network mesh size. The position of the maxima was found to be sensitive to concentration and annealing time and temperature. The scattering curves of the low concentration solutions could again be fitted using a plain-rod model. A thickness of ~ 7 nm was found in this case. FEFEFKFK samples seems to form fiber of the same diameter as the AEAEAKAK samples but in this case the fibers are able to aggregate or entangle and form a 3D network resulting in the formation of an hydrogel. Similar results were obtained for the FEFKFEFK samples and when glutamic acid (E) is replaced by aspartic acid (D).

When arginine (R) is used to replace lysine (K) large differences are observed in the scattering patterns. As shown in figure 4 a maximum is observed in the Kratky representation for the FDFRFDJR sample at 30 mg ml⁻¹. This curve suggests the presence, as for the AEAEAKAK samples of rod-like structures but with a larger diameter. Fitting the curves has not been possible yet as the low q part of the scattering pattern is missing. At lower concentration no structure seems to form.

Conclusion

This work has shown the importance of peptide sequence and type on the self-assembling properties and hydrogel formation. Results are still being analyzed in order to extract additional information like the linear mass of the fibers. Additional experiments at low q are required for some of the peptide.

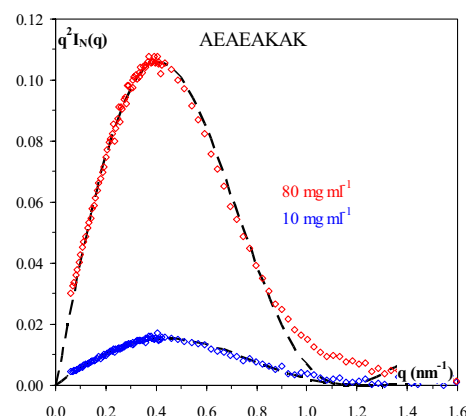


Figure 2: Intensity scattered by AEAEAKAK solutions.

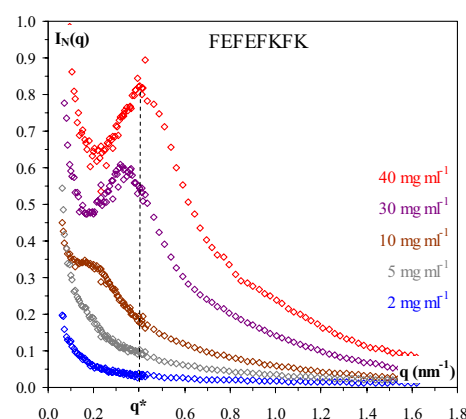


Figure 3: Intensity scattered by FEFEFKFK samples.

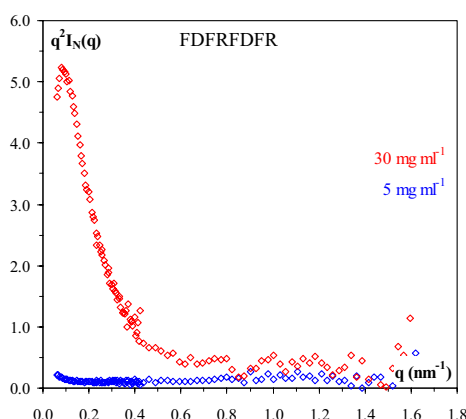


Figure 3: Intensity scattered by FEFEFKFK samples.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-019		
Experiment title:	SANS Investigation of bi-continous microemulsions in presence of sticker polymers		
Dates of experiment:	27.08.2005	Date of report:	17.03.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus Gaetano Mangiapia	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich, and Dipartimento di Chimica, University Napoli, 80126 Napoli, Italy		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Amphiphilic diblock copolymers were the first polymers found to increase the efficiency of surfactants in microemulsions dramatically (polymer boosting effect). The idea of amphiphilicity has been brought to an extreme by the new sticker polymers. Only a short hydrophobic C_{10} sticker is connected to the hydrophilic E_{100} block, a polymer of 100 ethylene oxide units. The questions arising for this new polymer are: (1) Is this unbalanced amphiphile still fully active at the membrane, i.e. does this polymer decorate the surfactant film as the diblock copolymer? (2) Does the polymer increase the efficiency equally well as the diblock copolymers (with respect to the polymer mass)? (3) Does the imbalance have any effect at all?

Prior to the neutron scattering experiments phase diagram measurements have been made. Here the one phase region of the bicontinuous microemulsion was determined. In a temperature vs. surfactant amount plot the one phase region looks like a fish tail, and the fish body is the 3-phase coexistence region. Both regions are connected in one point, the fish tail point, where the surfactant fails to dissolve the equal amounts of oil and water. The efficiency of a surfactant is measured by this minimum amount of surfactant γ_{ftp} . Plotting this γ_{ftp} as a function of the rescaled polymer amount $\sigma \cdot R_{ee}^2$, one obtains a measure for the sensitivity of the boosting effect, which can be compared to diblock copolymers. With respect to the total amount of polymer, the polymer boosting is comparable to diblock copolymers. This result agrees well with Lipowsky's theory [1].

The second measure is the temperature at the fish tail point. For symmetric diblock copolymers this temperature stayed constant within the accuracy due to the symmetry of the system. For the new sticker polymers this temperature increased with growing polymer amount. The imbalance of the polymer causes some spontaneous curvature which is balanced by the increased temperature. The sensitivity of this effect agrees well with Lipowsky's theory [1].

The macroscopically determined phase diagram is connected to microscopically defined parameters of the Helfrich model. The model assumes the elastic properties of the surfactant film to be dominant in the free ener-

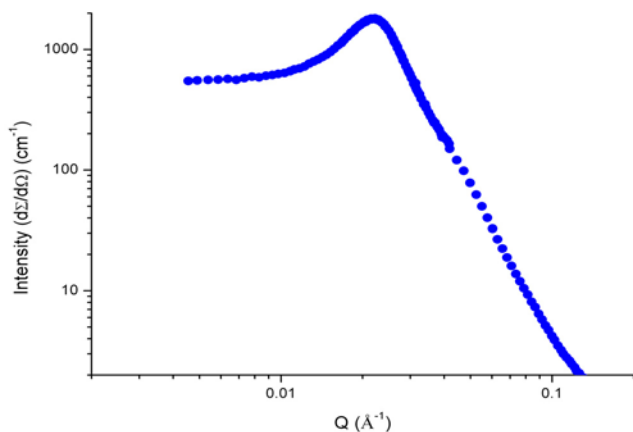


Figure 1: A typical SANS curve: Macroscopic cross section as a function of the scattering angle Q . The peak position $\sim 2\pi/d$ is connected with the domain size d , while the peak width $\sim 1/\xi$ is inversely proportional to the correlation length.

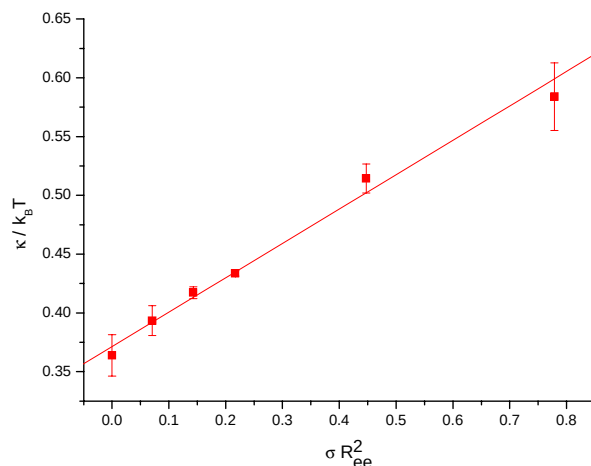


Figure 2: The obtained bending rigidity κ as a function of the scaled polymer amount. Using the Gaussian random field theory κ is related to the structural parameters according to $\kappa/k_B T = 0.85 \xi/d$. The slope measures the sensitivity of the polymer effect, and is comparable to diblock copolymers.

gy of the microemulsion. The three important parameters are the spontaneous curvature c_0 , and two elastic moduli, namely the bending rigidity κ and the saddle splay modulus $\bar{\kappa}$. The spontaneous curvature decreases with increasing temperature and increases with increasing sticker polymer amount. At the fish tail point the spontaneous curvature is zero, so the two contributions are balanced. The elastic moduli are spatially renormalized parameters with a logarithmic dependence on the surfactant amount. The absolute values of the elastic moduli increase with increasing polymer amount. At the fish tail point the saddle splay modulus is a negligible constant, and so the renormalization is balanced with the polymer term. This balance leads to an exponential dependence of the minimal surfactant amount with respect to the scaled polymer amount.

In theories the moduli κ and $\bar{\kappa}$ behave extremely similar, just the signs of the moduli are opposite ($\kappa > 0$ and $\bar{\kappa} < 0$). Thus a quantitative comparison of the macroscopically determined $\bar{\kappa}$ with κ is desired. Small angle neutron scattering experiments determine the domain structure if bulk contrast is chosen. A typical SANS pattern is shown in figure 1. One obtains the domain size d and the correlation length ξ , which are connected to the bending rigidity $\kappa/k_B T = 0.85 \xi/d$ according to the Gaussian random field theory. Three different surfactant amounts were measured in the one phase region for each polymer amount. For each polymer amount an inter-/extrapolation of κ was made to a constant surfactant amount; thus, the spatial renormalization does not play a role anymore. The directly measured bending rigidity κ as a function of the polymer amount is depicted in figure 2.

The sensitivity of both moduli on the polymer amount agree quantitatively between the sticker polymer and the diblock copolymer. Thus, the used amount of polymer is dominant for the efficiency boosting. The cheaper and biodegradable sticker polymers would exchange the diblock copolymers in applications.

The detailed comparison of the sensitivities between the real measurements and theoretical predictions show a 1.5 (to 2) times more sensitive behavior of the experimental systems. This might be due to the structure of real polymers and also due to confinement effects. More interesting is the agreement between the sensitivity of both moduli as predicted by the theory. While these monofunctional sticker polymers have the same effect on κ and $\bar{\kappa}$, some starlike polymers with higher functionality might imbalance the sensitivity of the two moduli. Bifunctional polymers are already investigated (KW2-05-031, KW2-05-036, KW2-05-046, KW2-05-049), and higher functionalities remain an interesting subject for applications in the future.

References:

[1] C. Hiergeist, R. Lipowsky, *J. Phys. II France* **6**, 1465 (1996)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-020		
Experiment title:	Determination of the structure of chitosan and poly(vinylpyrrolidone) hydrogels in the presence of anionic surfactants		
Dates of experiment:	28/08/2005	Date of report:	15/12/2005
Experimental team:			
Names	Addresses		
Gaetano Mangiapia	IFF – Neutronenstreuung, Forschungszentrum Jülich GmbH, D-52425 Jülich Tel. +49 2461 61 6048 (g.mangiapia@fz-juelich.de)		
Henrich Frielinghaus	IFF – Neutronenstreuung, Forschungszentrum Jülich GmbH, D-52425 Jülich Tel. +49 2461 61 5093 (h.frielinghaus@fz-juelich.de)		
Local Contact:	G. Mangiapia		

Experimental report text body

Chitosan [CHT] is a polycationic biopolymer obtainable from partial enzymatic or alkaline deacetylation of chitin, a natural and abundant polysaccharide occurring in crustaceous shells, insect exoskeletons and in associations with proteins and minerals. The good biocompatibility, natural availability, and the excellent physical, chemical and mechanical properties shown by CHT, make it a good candidate for using in medical field, as component in cosmetic products, agriculture and in water treatment. One of the most attractive features of CHT that has captured the attention of researchers from both academic and industrial areas, is the capability to form semirigid films and hydrogels with good swelling properties. This characteristic, together with its cationic nature, has allowed forming swellable pH-sensitive CHT gels used as stomach-targeted drug delivery systems, and CHT complexes useful in gene delivery applications.

In order to create new biomaterials with more helpful characteristics, CHT is often used as blend with other polymers and/or in combination with surfactants. The use of polymer blends allows, in principle, having new gels with properties which are different to those of single components, whereas polymer surfactant complexes, where present, can significantly modify the characteristics of solutions and hydrogels (for instance improved swelling properties), opening new possibilities of applications.

The purpose of this research project has been to perform a structural characterization of CHT and CHT/poly(vinylpyrrolidone) [PVP] hydrogels, obtained by means of SANS measurements. Furthermore, in order to create hydrophobic domains within the gel, that can in principle be used to dissolve lipophilic drugs, CHT and CHT/PVP gels have also been investigated in the presence of sodium decylsulfate [C10OS], one of the most widespread anionic surfactants.

Figure 1 reports scattering cross sections $d\Sigma/d\Omega$ for CHT and CHT/PVP hydrogels in D_2O . The scattering profile of both systems can be described in terms of the average distance between crosslinks (the mesh size ξ) arising from the thermal fluctuations of the polymer concentration, and in terms of the correlation distance ζ among polymer rich domains. With the hypothesis $\zeta \gg \xi$, the scattering cross section can be expressed as a sum of a lorentzian function that takes into account of the thermal fluctuations, and of an “excess term” describing the presence of inhomogeneities inside the hydrogel structure

$$\frac{d\Sigma}{d\Omega} = \frac{S_{oz}}{1 + q^2 \xi^2} + \frac{S_{ex}}{(1 + q^2 \zeta^2)^2} + \left(\frac{d\Sigma}{d\Omega} \right)_{inc} \quad (1)$$

where $(d\Sigma/d\Omega)_{inc}$ represents the incoherent contribution to the cross section measured. By fitting eq. (1) to the experimental data it has been possible to estimate both the parameters ξ and ζ (see table 1).

With the aim to investigate a possible interaction among polymeric chains forming the hydrogel structures and C10OS micelles or micelle-like aggregates, SANS measurements of CHT and CHT/PVP hydrogels have been performed in mixtures of H_2O/D_2O and in the presence of fully deuterated C10OS [DC10OS], in order to observe scattering arising only from the surfactant. Figure 2 reports scattering cross sections obtained for CHT and CHT/PVP hydrogels in the presence of DC10OS (0.1 mol kg^{-1}) in a mixture H_2O/D_2O such to make null the scattering contribution due to the hydrogels. For comparison it has also been reported $d\Sigma/d\Omega$ values for C10OS (0.1 mol kg^{-1}) in D_2O ; furthermore, for a better comparison, data of figure 2 have been multiplied for a scale factor. Inspection of the figure reveals the presence of a single broad maximum, characteristic of micellar systems where significant correlations between micelles or micelle-like aggregates are present. Moreover, the position of the maximum in $d\Sigma/d\Omega$ occurs at the same value of the scattering vector modulus q ($\approx 0.073 \text{ \AA}^{-1}$), indicating that a similar correlation distance exists among all the aggregates, and suggesting a lack of interaction between micelles and polymeric chains. On those bases, in order to extract structural information about the aggregates, systems have been modeled as a collection of charged prolate ellipsoidal micellar aggregates. From the fitting it has been possible to extract the micellar aggregation number N_{agg} , the actual charge z , the major and minor semiaxis of the hydrophobic core a and b , and the thickness of the hydrophilic shell δ . Table 2 reports the values of these parameters for the systems investigated, and from its inspection it is possible to note similar values obtained for all the systems, except for the value of the charge z . Micellar actual charge of systems containing hydrogels is sensibly reduced, probably because of the presence of residual positive charges on chitosan backbone that should shield C10OS aggregates. According with these results micelles of decylsulfate are free to move inside the polymeric gel, and could be in principle used as carriers for lipophilic drugs.

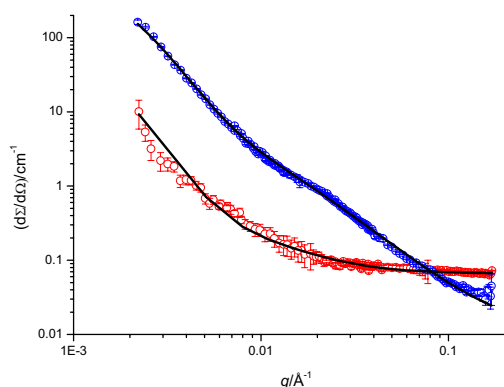


Figure 1 – Scattering cross sections obtained at 25°C for hydrogels of CHT (–) and CHT/PVP (–) in D_2O . Curves obtained from the fitting of the model described in the text are also reported.

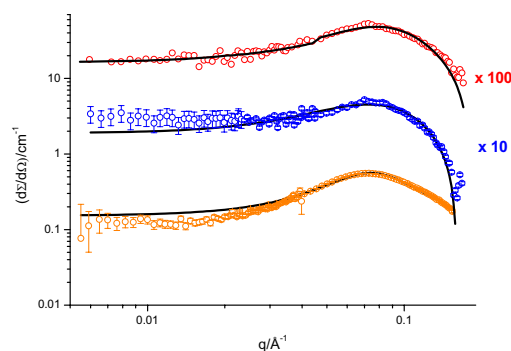


Figure 2 – Scattering cross sections obtained at 25°C for C10OS (–) in D_2O and for DC10OS in the presence of CHT (–) and CHT/PVP (–) hydrogels in mixtures H_2O/D_2O . In all the systems the concentration of surfactant is 0.1 mol kg^{-1} . Curves obtained from the fitting of the model described in the text are also reported.

	$\xi/\text{\AA}$	$\zeta/\text{\AA}$
CHT	96 ± 2	548 ± 10
CHT/PVP	85 ± 9	850 ± 40

Table 1 – Mesh size ξ and inhomogeneity distance ζ for CHT and CHT/PVP hydrogels in D_2O obtained from the fitting of the model described in the text.

	N_{agg}	z	$a/\text{\AA}$	$b/\text{\AA}$	$\delta/\text{\AA}$
C10OS	46 ± 2	-35 ± 2	15.3 ± 1.2	14.1 ± 0.5	3.4 ± 0.2
DC10OS/CHT	49 ± 3	-8 ± 1	16.2 ± 0.9	14.1 ± 0.5	3.5 ± 0.1
DC10OS/CHT/PVP	44 ± 2	-10 ± 2	14.6 ± 1.0	14.1 ± 0.5	3.4 ± 0.1

Table 2 – Micellar parameters obtained for C10OS in D_2O and for DC10OS in the presence of CHT and CHT/PVP hydrogels in contrast match mixtures H_2O/D_2O . In all the systems the concentration of surfactant is 0.1 mol kg^{-1} . The table reports the aggregation number N_{agg} , the actual charge z , the major and minor semiaxis of the hydrophobic core a and b respectively, and the hydrophilic shell thickness δ .



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-021		
Experiment title:	Effect of intercalation in sheet silicate on the conformation of poly(ethylene oxide)		
Dates of experiment:	19.08. – 20.08.2005	Date of report:	09.05.2006
Experimental team: Names	Addresses		
Helen E. Hermes Henrich Frielinghaus	IFF, FZ-Jülich IFF, FZ-Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

PEO-MMT interactions have been studied for many years¹. Interest has intensified recently due to the model nature of the system for studying confined chains, and hopes that it may be a suitable candidate for solid-state batteries². The indirect techniques IR and NMR have been used to examine the chain conformation of the intercalated PEO. X-ray scattering has also been widely used. From the results from these techniques and theoretical calculations, no consensus as to the conformation of PEO has been reached. The aim of these experiments was to determine using SANS the conformation of highly confined PEO chains.

We used solution intercalation to prepare composites of poly(ethylene oxide) (PEO) and sodium montmorillonite. X-ray scattering and differential scanning calorimetry measurements confirmed that using this sample preparation method and a suitable composition, it is possible for all the PEO to be intercalated between the silicate layers. The thickness of the intercalated PEO layers is 0.815 nm and extremely constant.

In this initial experiment we investigated a series of 6 samples with fixed montmorillonite content and fixed polymer molecular weight plus a reference h-d PEO blend. In the montmorillonite-PEO mixtures, the relative amounts of h-PEO and d-PEO were varied such that the average scattering length density of the polymer phase was varied around the scattering length density of the montmorillonite.

Figure 1 illustrates the data obtained from these SANS measurements at 20m detector distance. At these lowest Q values the contrast change must have the largest effect, but obviously no considerable trends are observed. Theoretically we expect the contrast match at ~50% deuterated content. Since all samples remain white after the freeze drying and pressing, still there must be a lot of air bubbles. Thus, the scattering from the air is dominating the obtained spectra independent of the selected contrast.

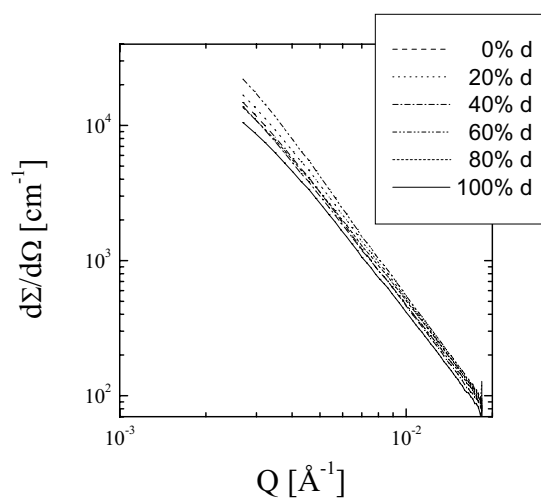


Figure 1: Scattering intensities of a contrast variation experiment on a PEO/MMT nanocomposite. The content of deuterated PEO was varied between 0 and 100%. Theoretically at ~50% the system should be contrast matched, and the chain scattering should be visible. Practically, no considerable change of the intensity is observed. All samples are white after the preparation, and so many air bubbles must be responsible for the observed scattering pattern independent of the selected contrast.

In latest experiments we changed the sample preparation from freeze drying to slowly drying (solvent casting), and first experiments looked more promising. T. Zacherle will obtain in the near future the full information about the scattering of confined PEO chains in montmorillonite clay sheets.

References

1. B.K.G. Theng, "Formation and properties of clay-polymer complexes", Elsevier Scientific, Oxford, 1979
2. P. Aranda, E. Ruiz-Hitzky, *Chem. Mater.* **4**, 1395-1403 (1992)
3. Experimental report KW1-04-025



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-023		
Experiment title:	Influence of temperature and solvent on the phase behaviour of $\text{Co}(\text{AOT})_2$ –containing nonionic microemulsions		
Dates of experiment:	1.09 – 4.09.05	Date of report:	14.03.06
Experimental team: Names	Addresses		
Feygenson Mikhail, Pollmeier Klaus, Kentzinger Emmanuel Dr.,	Forschungszentrum Jülich GmbH Institut Für Festkörperforschung (IFF-STM) D-52425 Jülich Germany		
Sager Wiebke Dr.	Forschungszentrum Jülich GmbH Institut Für Festkörperforschung (IFF-IWM) D-52425 Jülich Germany		
Local Contact:	Dr. Henrich Frielinghaus		

Experimental report text body

For the synthesis of the Co nanoparticles we employed the interior of water-in-oil (w/o) microemulsions as nanoreactors, as originally proposed by Pileni et.al.(1999). In their early paper Pileni and coworkers used w/o microemulsions that were stabilized by NaAOT (sodium 2- diethylhexylsulfosuccinate), whereby the Co^{2+} -delivering microemulsion contained additionally $\text{Co}(\text{AOT})_2$ and water and the second microemulsion that delivered the reducing agent NaBH_4 contained only NaAOT and the aqueous NaBH_4 -solution. In this way, particle size and polydispersity could be adjusted by the water-to-surfactant ratio (w/s) and the molar ratio between Co^{2+} and NaBH_4 . The major problem of this approach, was the low yield of Co nanoparticles. In recent papers Pileni et al. used, therefore, a microemulsions stabilized by $\text{Co}(\text{AOT})_2$ only to which they injected the aqueous NaBH_4 - solution. However, this synthesis route is less defined since the microemulsions phase separate upon addition of the NaBH_4 -solution.

In order to circumvent both the low yield of Co nanoparticles and undefined particle formation conditions due to phase separation, we explored a synthesis route in which we employed w/o microemulsions that are stabilized by the nonionic surfactants of the ethoxylated alkyl- or arylether series such as C_{12}E_5 and Igepal CO520 and contain the NaBH_4 -solution. Co nanoparticle formation is then induced by injecting a solution of $\text{Co}(\text{AOT})_2$ in hexane. In order to characterize the morphology of the microemulsions employed before and after addition of $\text{Co}(\text{AOT})_2$, we performed SANS measured of the microemulsions in shell contrast at KWS-2 in August 2005. As can be seen from Fig. 1 the C_{12}E_5 stabilized microemulsions consist mainly of spherical droplets at high temperatures and transform only partially into cylinders at low temperatures within the one-phase region. However, Igepal stabilized microemulsions display a substantial cylinder fraction already at high temperatures and show the characteristic scattering from long cylinders at low temperatures (Fig.2). To mimic the 1 M NaBH_4 -containing microemulsions we used 1.2 M NaCl-solutions as aqueous phase (Fig.3). Addition of $\text{Co}(\text{AOT})_2$ lead similar to NaAOT to a cylinder-to-sphere transition.

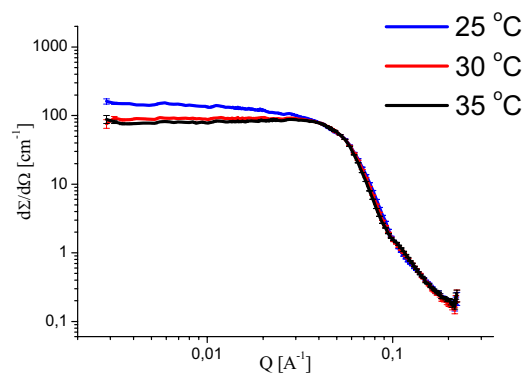


Fig 1: 13.6% $C_{12}E_5$, $w/s=0.5$, 1.2 M NaCl

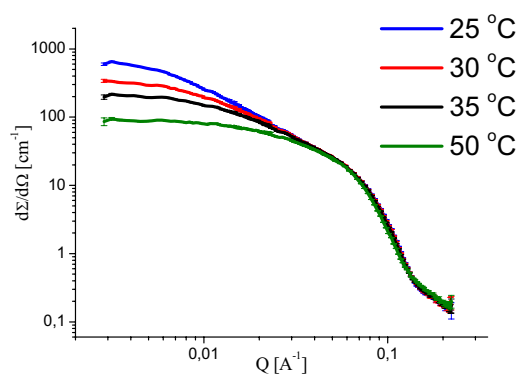


Fig 2: 13.6% Igepal, $w/s=0.2$, 1.2 M NaCl

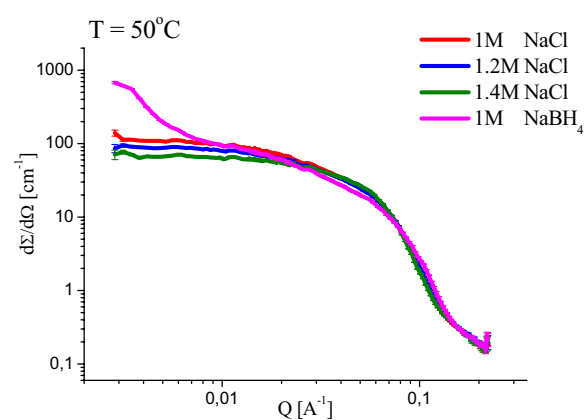


Fig 3: 13.6% Igepal, $w/s=0.2$

We also measured the temperature dependence of the Igepal and $C_{12}E_5$ stabilized microemulsions at different water-to-surfactant ratio.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-025		
Experiment title:	Critical fluctuations and absorption of individual fluids confined in porous media: continuation		
Dates of experiment:	21.-25. Feb. 2006	Date of report:	31. May 2006
Experimental team: Names	Addresses		
G. Rother ¹ Y. Melnichenko ¹ G.D. Wignall ¹	¹ Center for Neutron Scattering, Oak Ridge National Laboratory, 1 Bethel Valley Rd, Oak Ridge, TN 37830, USA		
Local Contact:	H. Frielinghaus		

Experimental report text body

The experiment aimed to study the adsorption from supercritical and sub critical d-propane to silica aerogel. Measurements have been performed at the KWS2 instrument using a home-built pressure cell. First we studied the bulk properties of d-propane in the vicinity of the critical point. By performing pressure scans at different temperatures we determined the critical temperature of d-propane at $T_c = 91.0^\circ\text{C}$, thus being shifted by 6.6 K towards lower temperatures with respect to h-propane. The critical pressure of bulk d-propane is at $p_c = 616$ psi, being the same as found in h-propane. After filling the pressure cell with silica aerogel (porosity 96%) pressure scans have been performed at temperatures of 50°C , 88°C , 91°C , 96°C , 102°C and 150°C . Small Angle Scattering data have been collected in the Q-range $0.01 \text{ \AA}^{-1} \leq Q \leq 0.18 \text{ \AA}^{-1}$ with a typical measurement time of 2 – 10 min (simultaneous measurement of Transmission data). We found strong alterations in the SANS and Transmission data with variation of pressure. Figure 1 shows the results of a pressure scan at the (bulk) critical temperature. These actual data are viewed in comparison to the calculated data for a two-phase system, in which we assume that the pores are evenly filled with nonadsorbed fluid of the respective density. We find strong deviations of our experimental data from the two-phase model in both small angle scattering and transmission. In our adsorbed phase model we assign all of these deviations to the existence of an adsorbed phase that comprises the third phase besides the silica aerogel and nonadsorbed fluid. The three-phase model of Wu (Polymer 1982) is employed to relate the invariant obtained from SANS data to volume fractions and scattering length densities of the three phases. Using a formalism that combines small angle scattering and transmission results we can readily calculate the volume fraction and density of this adsorbed phase without further model assumptions. The results of this calculation for the critical temperature are shown in figure 2.

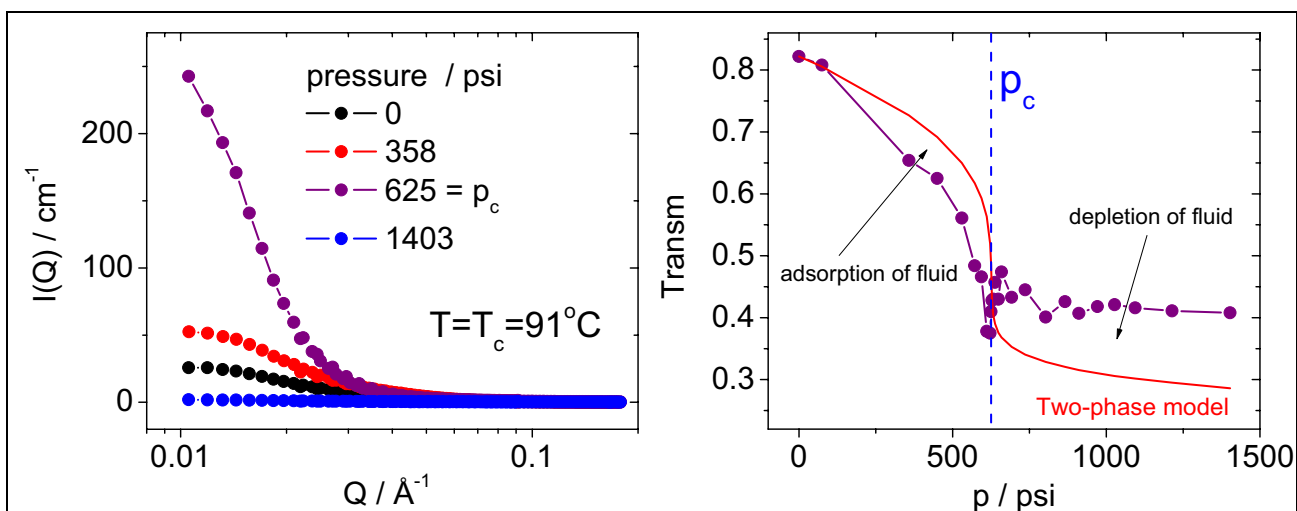


Figure 1: Results from a pressure scan at the critical temperature; left figure: SANS data, right figure: Transm.

The results give a detailed picture of the physical state of the pore liquid. We find the formation of a densified adsorbed layer at low densities, which reaches a maximum density of about 0.7 g/ml, being the density of liquid d-propane. The adsorbed layer fills the entire pore space at low and high densities. In the regime of medium densities our model suggests the breakdown of the adsorbed layer. At high densities we find depletion of fluid from the pore space. The third phase is now a low-density phase with a high volume fraction. Our findings are in general agreement with earlier findings of Findenegg and others, which found negative values of excess adsorption of fluids at high densities. In the future we plan to study the transition from the high-density adsorbed layer to the low density depletion layer in more detail.

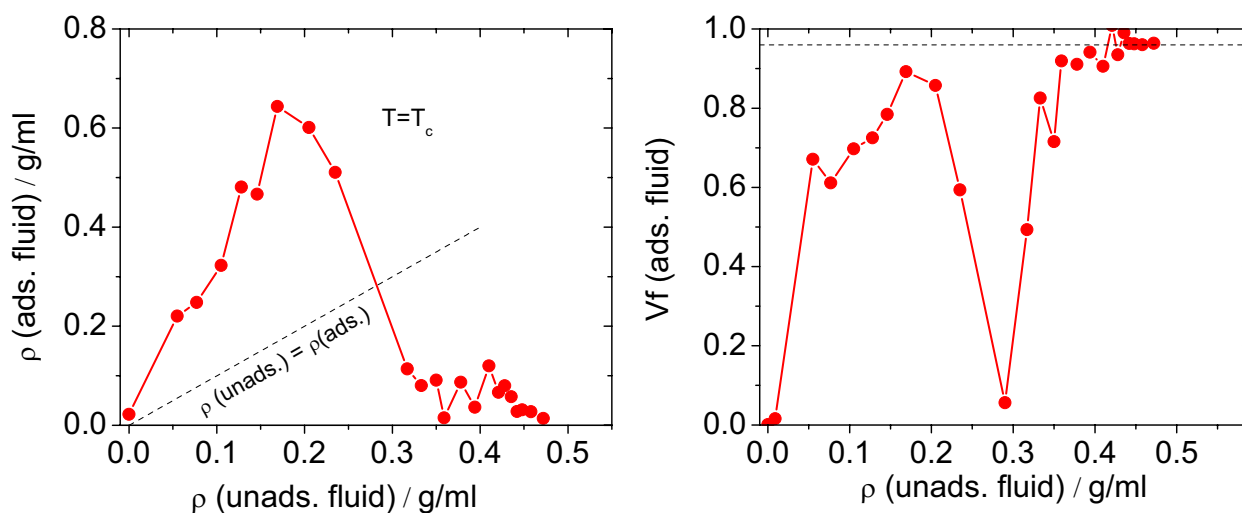


Figure 2: Physical properties of the adsorbed phase as a function of the density of unadsorbed fluid, shown for the critical temperature; left figure: density of adsorbed fluid, right figure: volume fraction of adsorbed fluid.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-026		
Experiment title:	Struktur des denaturierten Proteins Rnase A		
Dates of experiment:	Sep. 2005	Date of report:	Mai 2006
Experimental team: Names	Addresses		
Ralf Biehl Bernd Hoffmann Michael Monkenbusch Rudolf Merkel Dieter Richter	FZJ/IFF FZJ/ISG FZJ/IFF FZJ/ISG FZJ/IFF		
Local Contact:	Aurel Radulescu		

Experimental report text body

The protein folding and function is strongly coupled to the structure and the thermal equilibrium fluctuations. In view of the macromolecule energy landscape the protein folding follows a path from the unfolded state at high energy to the low energy state at the final configuration with intermediate states in between. Thereby the secondary and ternary structure is determined. Catalytic activities or transport mechanisms follow transitions between intermediate states in the energy landscape. All involve configurational changes on length scales from single amino acids to sizes of complete α helices or β sheets and the total size of the protein. Timescales reach from picoseconds to microseconds. A way to explore the energy landscape at equilibrium is to observe thermal fluctuations of the protein. By changing environmental parameters e.g. temperature the level of energy is changed.

Here as a starting point for our dynamical experiments we want to determine the structural changes of the protein during unfolding by temperature increase. The protein was examined under conditions providing the possibility of refolding to the natural state.

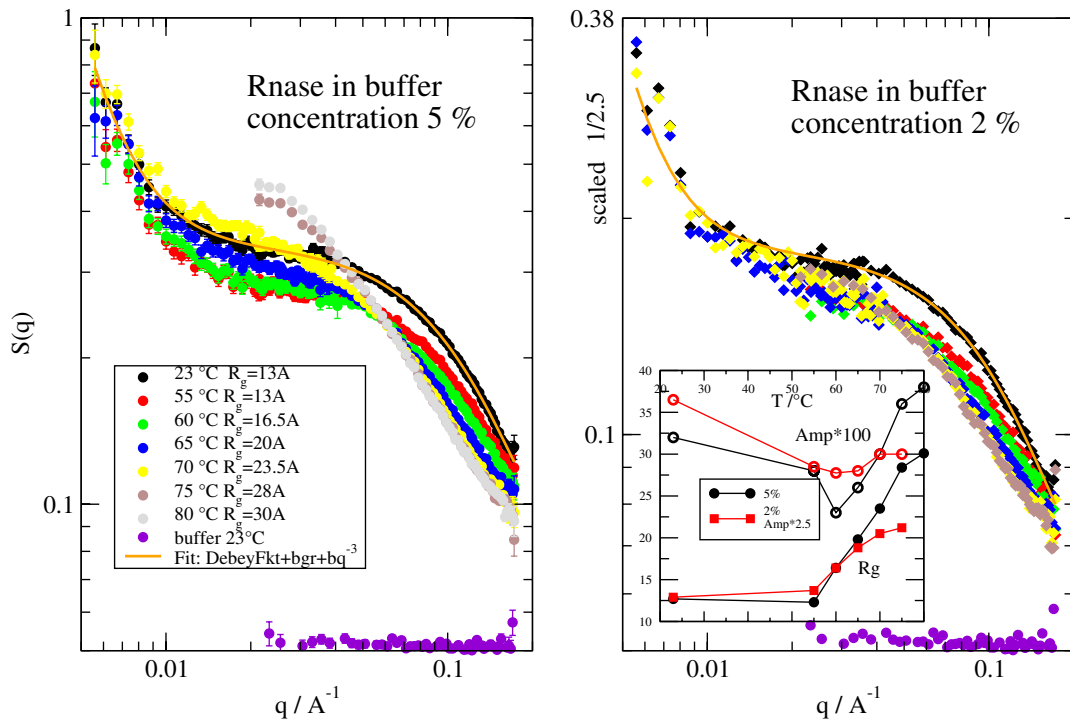


Figure 1: Sans Scattering data for different temperatures. Left: concentration of 5%, right: concentration of 2%. The inset in the right graph shows the radius of gyration and the intensity of a fit according to the debey formula including background and a power law q^{-3} .

Figure 1 shows the result of our measurements. Both concentrations show the same main features. At low q we observe an increasing intensity due to aggregates or dirt. We modeled this in our fits by a power law $\sim q^{-3}$. At higher q we observe the typical plateau with decreasing intensity to highest q . As we expect the protein to unfold from its globular shape with increasing temperature, we have chosen a Debye function to model this even for the unfolded state. The Debye function

$$S(q) = 2 * (\exp(-q^2 R_g^2) - 1 + q^2 R_g^2) / q^4 R_g^4 \quad 1$$

is commonly used to describe a Gaussian distribution of point scatterers (eg. a free Gaussian chain) and is used here only to have a consistent model to evaluate the radius of gyration. To include the significant amount of aggregates and/or dirt inside the sample we add a power law q^{-3} . Also a constant background is assumed to account for the solvent scattering. As the orange curve in both plots shows this model describes our data well and gives similar results for both concentrations.

The inset in figure 1 shows the parameters of the resulting fits. From room temperature to 55 °C we observe no significant change in R_g . Above the protein unfolds from $R_g = 13\text{\AA}$ to $R_g = 22\text{\AA}$. At a concentration of 5% the increase at temperatures above 65 °C is much higher. Comparison of the original data in the left graph show a significant increase and a change of the overall shape which we cannot observe for a concentration of 2%. We conclude that the increase of the scattering intensity is due to gel formation at highest temperature and concentration.

The 2% sample data will be compared to NSE and DLS data measured on the same protein . We will restrict our further experiments to Temperatures without gel formation.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-027		
Experiment title:	Shear-induced structural changes of HM-alginate in the presence of poly- β -cyclodextrin -an <i>in situ</i> Rheology and SANS study		
Dates of experiment:	26/09/2005	Date of report:	27/05/2006
Experimental team: Names	Adresses		
Reidar Lund Bo Nyström Anna-Lena Kjørnksen	DIPC, University of Basque Country, Spain Dep. of Chemistry, University of Oslo, Norway. Dep. of Chemistry, University of Oslo, Norway		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

β -cyclodextrins (β -CD) is a cyclic polysaccharide, it is cone-shaped consisting of a hydrophobic core that can encapsulate hydrophobic groups, and a hydrophilic external surface. In mixtures of hydrophobically modified polymers (e.g. HM-alginate) and β -CD the deactivation of the hydrophobic moieties will result in a weaker tendency to form association complexes. In this case we will not observe any shear-induced effects. However, if we instead of β -CD add to the solution of HM-alginate poly- β -cyclodextrin (poly- β -CD) formation of bridges may occur. In this case a viscosification takes place and complex shear dependence is observed. A striking and novel feature here is that the shear thickening behaviour is observed at a fairly high shear rate (10 s^{-1}). The magnitude of this effect is strongly temperature dependent (see Figure 1). One conjecture is that by applying a shear flow, the alginates and/or poly β -CD are extended and this effect facilitates the development of bridges. This gives rise to the viscosity maximum observed in the shear rate curve. At higher shear rates this structure is disrupted, and a shear thinning behaviour appears.

In order to understand the rheological behavior we wanted to investigate structural changes induced under shear. For this purpose we employed a shear cell apparatus in the neutron beam and measured the structure factor over the whole Q-range accessible as a function of three different shear-rates, 2, 10, 50 s^{-1} . The scattering was initially detected continuously with some minutes interval (typically 10 min) by performing continuous scans at intermediate Q (8 m detector distance) while the shear was being applied. However, no time dependent features were found. Representative results showing the scattering curves over the whole Q-range (20, 8 and 2m detector distance) are given in Figure 2.

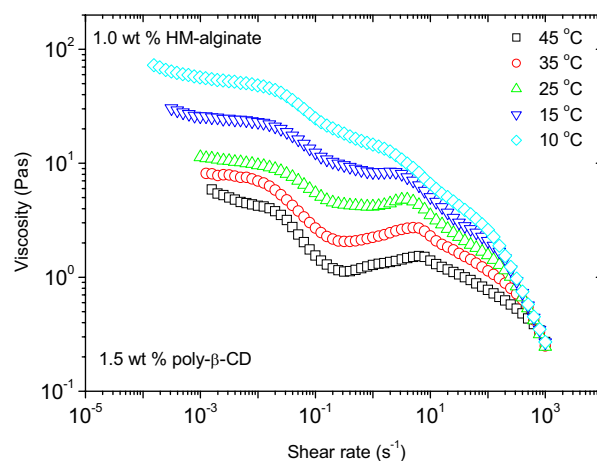


Figure 1. Shear rate dependence of the viscosity of a sample containing 1.0 wt % HM-alginate and 1.5 wt % poly- β -CD at different temperatures.

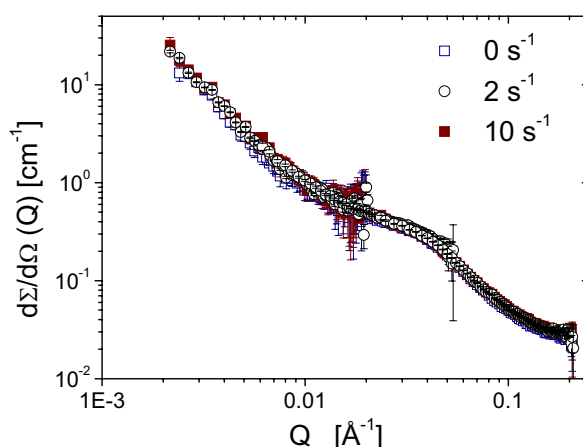


Figure 2. In situ Rheo-SANS results of the same HM-Alginate/poly- β -dextrin) mixture at different shear rates. 25 °C

As seen in the figure we observe no effect of shear on the overall scattering from the sample. This is rather intriguing as shearing of the sample has dramatic effects on the rheology. Indeed comparing with figure 1 we observe strong shear dependence and even a significant shear-thickening at relatively high shear rates (around 10 s^{-1}). Hence the results likely demonstrate that the structural changes occur on length scales much larger than the mesoscopic length scales covered by SANS (here approximately $300 - 3 \text{ nm}$). Similar findings have also been found for jammed soft star-like colloids of different arm numbers, where the rheology shows a rather rich behavior being undetected by SANS [1]. The main results of this experiment are part of an article published in *Biomacromolecules* [2].

REFERENCE:

1. Barbara Lonetti and Joerg Stellbrink *Private communication*
2. Virginie Burckbuchler, Anna-Lena Kjøniksen, Céline Galant, Reidar Lund, Catherine Amiel, Kenneth D. Knudsen and Bo Nyström *Biomacromolecules*, *in press*



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-028, KW2-05-051		
Experiment title:	Characterization of star-like micelles by contrast variation		
Dates of experiment:	12.11. - 14. 11.2005 15.02.2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink B. Lonetti	IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

We investigated the phase behaviour of star-like micelles formed by the amphiphilic block copolymer poly(ethylenepropylene)-poly(ethyleneoxide), $M_{w,PEP}=1000$ g/mol, $M_{w,PEO}=20000$ g/mol, in different water/dimethylformamide mixtures by small angle neutron scattering (SANS) [1] and partly by light scattering and rheology. Changing the solvent composition changes the aggregation number (or functionality), f , of the micelles due to changes in the interfacial tension between the core-forming, hydrophobic PEP and the solvent. This enabled us to construct the experimental equilibrium phase diagram in the packing fraction (η) / functionality (f) representation and compare it to theoretical predictions for regular star polymers, see fig.1. In particular the location of the fluid/solid phase boundary and the glass line was derived. Recently we synthesized a new PEP-PEO block copolymer with same molecular weight and block composition, but different H/D-labelling, i.e. protonated PEP and partially deuterated PEO. Moreover, this polymer has been prepared in larger amounts to be able to perform rheological and Rheo-SANS experiments also at higher volume fractions. As a first step we had to characterize the corresponding micelles with respect to their functionality f , radius of the hydrophilic shell, R_{shell} , and radius of the hydrophobic core, R_{core} . Prerequisite for such a characterisation is an exact determination of the experimental matching points by SANS contrast variation experiments.

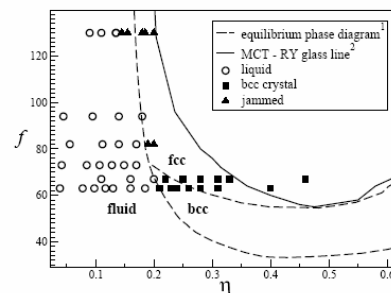
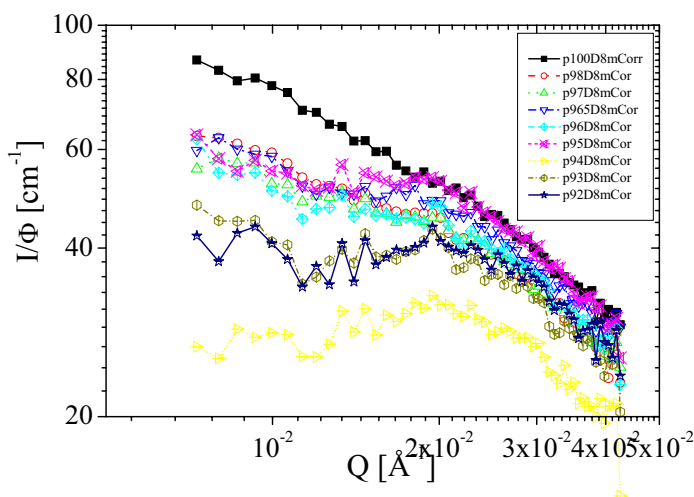


Figure 1: Experimental phase diagram of star-like micelles compared to theory.

In this experiment we investigated (very) dilute micellar solutions, $\Phi=0.25\%$, in different $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures. Besides the two pure isotopic solvents (“full contrast”) and an intermediate contrast with $\Phi_{\text{D}_2\text{O}}=50\%$, a detailed series of contrasts around the nominal core contrast, $\Phi_{\text{D}_2\text{O}}=96\%$ was investigated. Figure 1 shows the corresponding SANS curves obtained at KWS2. One has to keep in mind that the experiment is pushing the SANS instrument to its limits due to the low concentration and the small changes in contrast, but already by visual inspection one sees that the (expected) forward scattering resulting from the PEO corona shows a minimum for a solvent mixture with $\Phi_{\text{D}_2\text{O}}=95\%$. This is further confirmed by a more sophisticated data analysis using a core-shell form factor and taking into account all experimental uncertainties with respect to synthesis and characterisation of the used partially labelled diblock copolymer. Still under investigation is the question of preferred hydration/deuteration of the PEO corona in the H_2O -rich contrasts investigated.



References:

- [1] M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, *Phys. Rev. Letters*, **94**, 195504, 2005.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

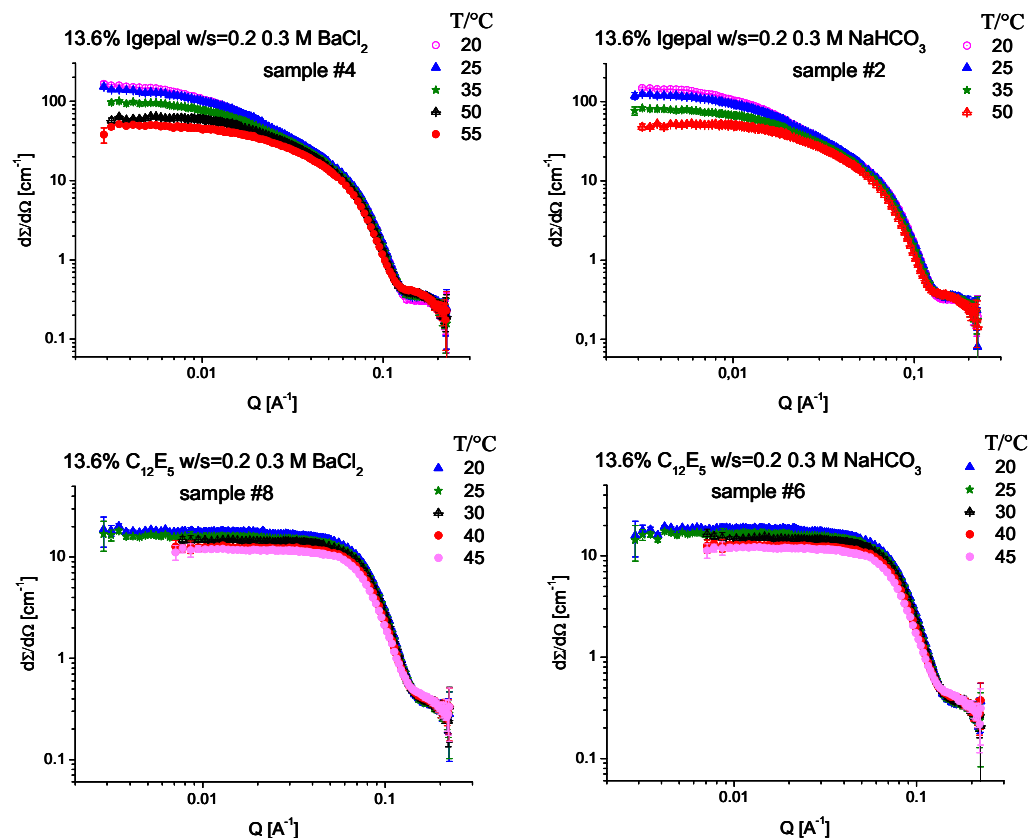
Proposal number:	KW2-05-030		
Experiment title:	Characterization of nonionic w/o microemulsions as precipitation media for the synthesis of BaCO ₃ nanoparticles.		
Dates of experiment:	September 19-20, 2005 November 1-2, 2005 December 2-3, 2005	Date of report:	Dec. 15, 05
Experimental team: Names	Addresses		
W.F.C. Sager	IFF-Soft Matter, FZ-Jülich P.O. Box 1913, 52425 Jülich		
M. Feygenson	IFF-8: Scattering Methods, FZ-Jülich P.O. Box 1913, 52425 Jülich		
Local Contact:	A. Radulescu		

Experimental report text body

In order to gain more insight into the "templating" role of the microemulsion, we studied in detail by transmission electron microscopy the formation of BaCO₃ nanocrystals within the one-phase region of different nonionic w/o microemulsions stabilized either by Igepal CO520 or C₁₂E₅. Inducing the precipitation of BaCO₃ by mixing two microemulsions, that differ only in the type of salt solubilised, allowed us to investigate, for the first time, the formation of nanoparticles within a large parameter space that comprises variations of the microemulsion composition, salt concentrations and temperature. A variety of nanostructures with well-defined morphology emerges ranging from (stacked) platelets, (self-assembling) rhombohedral nanocrystals, nano-needles, (ordered) hexagonal nanorods to nano-fibres and -bundles. Varying the conditions of the precursor microemulsions, therefore, permits to examine the transitions between the different nanostructures, e.g., transitions between needles and (hexagonal) nanorods, polygonal crystals and elongated rhombohedral crystals, systematically and to finally gain insight into the mechanisms of their formation. For the latter it is a prerequisite to know the morphology of the precursor microemulsions and to explore how changes in the morphology of the microemulsions are reflected in the nanostructures formed.

During our KWS2-beamtime in September and November we focused on characterising the microstructure of the microemulsions formed by either Igepal CO520 or C₁₂E₅ as a function of temperature and salt concentration (0.1-0.3 M) within the aqueous phase for a water-to-surfactant ratio of w/s=0.2. Fig. 1 shows the temperature series of the measured scattering curves for 0.3 M BaCl₂ and 0.3 M NaHCO₃, respectively. As can clearly be seen, microemulsion droplets stabilized by C₁₂E₅ are within the one-phase region much more stable against aggregation and cylinder formation upon lowering the temperature than for the Igepal stabilized microemulsions. By a first analysis of our data with the 2-component model for spheres and cylinders, developed earlier for the analysis of scattering curves of AOT stabilized microemulsions [1], we found that for the C₁₂E₅ system the volume fractions of spheres decrease from about 80% to 50% between 50 °C and 20 °C, almost independent of the salt concentration. Albeit more effort is still necessary on the improvement of our model it is already clear that the cylinders shorten drastically at salt concentrations above 0.3 M.

Fig. 1

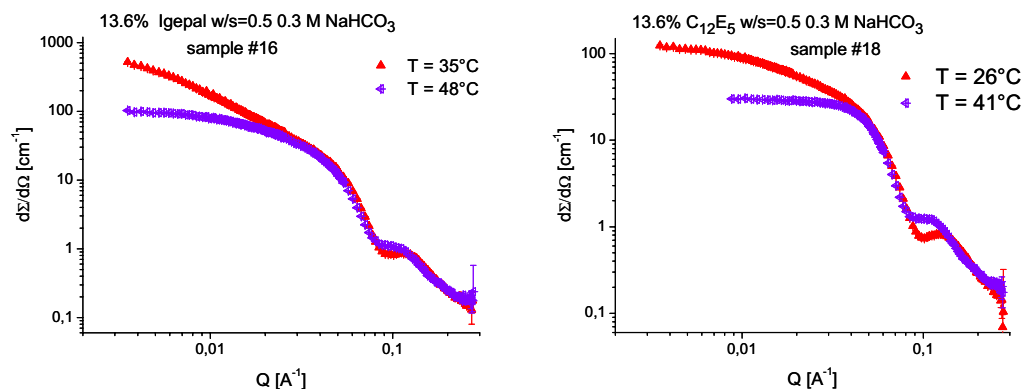


In the Igepal microemulsions, cylinders are already present in volume fractions of 40-60% even at the highest temperatures measured and reach volume fractions of 100% (far) above the lower phase boundary. An increase in the salt concentration has here only little effect on the cylinder length but reduces the number of cylinders significantly.

In December we started to extend our SANS study to higher w/s values and to also investigate microemulsions stabilized by mixtures of Igepal CO520 and C₁₂E₅. Fig. 2 shows scattering curves obtained just below the upper and just above the lower phase boundary for Igepal and C₁₂E₅ microemulsions at w/s=0.5 for 0.3 M NaHCO₃. At this water-to-surfactant ratio the cylinder fraction and cylinder length increases also for C₁₂E₅ microemulsions strongly upon lowering the temperature.

[1] D.I. Svergun, P.V. Konarev, V.V. Volkov, M.H.J. Koch, W.F.C. Sager, J. Smeets, and E.M. Blokhuis, J. Chem. Phys. 113, 1651 (2000).

Fig. 2





Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-031, KW2-05-036, KW2-05-046, KW2-05-049		
Experiment title:	Bi-continuous microemulsions in presence of bifunctional sticker polymers – part I, II, III, IV		
Dates of experiment:	27. – 28.09., 27.10., 06. – 07.12.2005, 26.01.2006	Date of report:	21.03.2006
Experimental team: Names	Addresses		
Martin Brodeck Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

After successfully introducing monofunctional sticker polymers (KW2-05-019), the bifunctional sticker polymers were investigated to complete the picture of multi-arm sticker polymers. A theory of T. Auth and G. Gompper [1] predicted a 10% higher sensitivity with respect to the total number of anchored arms. Higher functionalities increase the sensitivity even further. The aim of the present study is an experimental check of the predictions of this theory. Two bifunctional sticker polymers with different sticker lengths were synthesized, namely a $C_{12}(E_{100})_2$ and a $C_{16}(E_{100})_2$. The full information of phase diagram and SANS measurements was collected and compared amongst each other, with the monofunctional sticker and with theory.

Prior to the neutron scattering experiments phase diagram measurements have been made. Here the one phase region of the bicontinuous microemulsion was determined. In a temperature vs. surfactant amount plot the one phase region looks like a fish tail, and the fish body is the 3-phase coexistence region. Both regions are connected in one point, the fish tail point, where the surfactant fails to dissolve the equal amounts of oil and water. The efficiency of a surfactant is measured by this minimum amount of surfactant γ_{ftp} . Taking the oil solubility of the surfactant into account one obtains the membrane content $\Psi \approx \gamma_{ftp} - 0.01$. Figure 1 shows the membrane content as a function of the scaled polymer content $\sigma \cdot R_{ee}^2$. The slope is measure for the strength of the polymer boosting effect. The monofunctional sticker polymer is an equally good booster as the diblock copolymer. The bifunctional sticker $C_{12}(E_{100})_2$ has the lowest effect. Three phase coexistence measurements yielded a high water solubility of this sticker – the $C_{12}(E_{100})_2$ is not fully active at the surfactant membrane. The $C_{16}(E_{100})_2$ on the other hand is almost not found in the water phase in agreement with the better boosting ability. Nonetheless, the $C_{16}(E_{100})_2$ is a worse booster as the monofunctional sticker.

The second measure is the temperature at the fish tail point. The imbalance of the unsymmetric polymers causes some spontaneous curvature which is balanced by the increased temperature. A similar picture is obtained as for the sensitivity of the membrane content Ψ . The details are not discussed in the present paper.

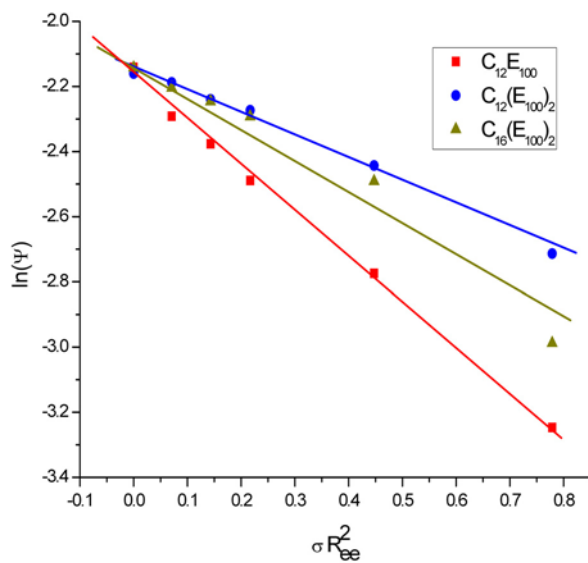


Figure 1: The minimum amount Ψ of surfactant needed to solubilize equal amounts of water and oil as a function of the scaled polymer amount. The monofunctional $C_{12}E_{100}$ sticker has a comparable boosting to the diblock copolymer, whereas the bifunctional sticker polymers are considerably weaker.

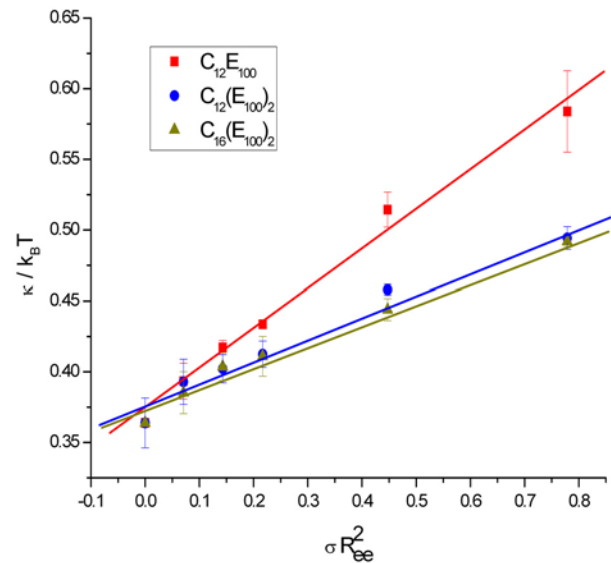


Figure 2: The by SANS measured bending rigidity κ as a function of the scaled polymer amount. The monofunctional sticker has a comparable sensitivity as a diblock copolymer. Both bifunctional sticker polymers have a considerably weaker sensitivity. This result in comparison with the theory remains an open question.

The macroscopically determined phase diagram is connected to microscopically defined parameters of the Helfrich model. The model assumes the elastic properties of the surfactant film to be dominant in the free energy of the microemulsion. The three important parameters are the spontaneous curvature c_0 , and two elastic moduli, namely the bending rigidity κ and the saddle splay modulus $\bar{\kappa}$. The spontaneous curvature decreases with increasing temperature and increases with increasing sticker polymer amount. At the fish tail point the spontaneous curvature is zero, so the two contributions are balanced. The elastic moduli are spatially renormalized parameters with a logarithmic dependence on the surfactant amount. The absolute values of the elastic moduli increase with increasing polymer amount. At the fish tail point the saddle splay modulus is a negligible constant, and so the renormalization is balanced with the polymer term. This balance leads to an exponential dependence of the minimal surfactant amount with respect to the scaled polymer amount.

In theories the moduli κ and $\bar{\kappa}$ behave extremely similar, just the signs of the moduli are opposite ($\kappa > 0$ and $\bar{\kappa} < 0$). Thus a quantitative comparison of the macroscopically determined $\bar{\kappa}$ with κ is desired. Small angle neutron scattering experiments determine the domain structure if bulk contrast is chosen. One obtains the domain size d and the correlation length ξ , which are connected with the bending rigidity $\kappa/k_B T = 0.85 \xi/d$ according to the Gaussian random field theory. Three different surfactant amounts were measured in the one phase region for each polymer amount. For each polymer amount an inter-/extrapolation of κ was made to a constant surfactant amount; thus, the spatial renormalization does not play a role anymore. The directly measured bending rigidity κ as a function of the polymer amount is depicted in figure 2. Again, the two bifunctional sticker polymers are much weaker than the monofunctional sticker. The monofunctional sticker polymer has a comparable sensitivity as the diblock copolymer.

The general picture about sensitivities of κ and $\bar{\kappa}$ is consistent within the measurements. The monofunctional sticker works equally well as efficiency booster compared to the diblock copolymer. The bifunctional sticker polymers do not work as effectively as the simple sticker. Measuring the activity of the polymer in the three phase coexistence states that the $C_{12}(E_{100})_2$ is not fully active, while the $C_{16}(E_{100})_2$ is supposedly strongly active. After the theory the bifunctional sticker polymers should be 10% stronger efficiency boosters. So the remaining question is if the theory is wrong, or if the activity measurements are interpreted wrongly, since this method is indirect.

[1] T. Auth, G. Gompper, *Phys. Rev. E* **68**, 051801 (2003)



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-033, KW2-05-038		
Experiment title:	Investigating the polarized GISANS method at KWS-2 – Part I and Part II		
Dates of experiment:	05.10. – 07.10.2005 04.11. - 06.11.2005	Date of report:	13.06.2006
Experimental team: Names	Addresses		
E. Kentzinger H. Frielinghaus Th. Brückel	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	H. Frielinghaus		

Experimental report text body

In order to investigate the polarized GISANS method, we measured polarized GISANS signal from a remanent polarizing supermirror, a system already studied by off-specular scattering on HADAS. The aim of this investigation was to have access to the correlation length of the structural and magnetic correlations, all smaller than the ones that can be probed on a reflectometer like HADAS. An un-polarized GISANS measurement was performed before on the same system (report KW2-05-003).

For this measurement, we used the set-up depicted in Fig.1 of report KW2-05-032. Some of the results obtained are depicted in Fig.1. In that picture, we show the GISANS signal measured at fixed angle of incidence and for different positive values of the applied magnetic field after the sample was saturated in the minus direction. Each state is measured first with spin-down incoming neutrons (flipper off), then with spin-up incoming neutrons (flipper on). As the applied magnetic field is increased, the diffuse signal is progressively transferred from the spin-down channel to the spin-up one.

The measured signals can be explained by comparing them with the off-specular scattering measured on the same sample on HADAS. In Fig.2 we show such measurements performed at $\mu_0 H = 3.1$ mT, a field close to the 3.3 mT in Fig.1. In Fig.2 the positive α_f values spanned by the GISANS measurements are marked by red lines. The diffuse scattering at $(\alpha_i + \alpha_f)$ values below, around and above the specular $\alpha_i + \alpha_f = 3^\circ$ value in the spin-down and around the specular in the spin-up channel is scattering from the interfacial roughness correlations, as can be seen respectively in the I— and the I++ channels of Fig.2. The strong intensity around $\alpha_i + \alpha_f = 2^\circ$ in the spin-down channel is scattering by the magnetic correlations, as can be seen in the I+ channel of Fig.2. In this experiment, those correlations were not resolved, due to the too small collimation and sample-to-detector lengths. A tentative to resolve those long-range correlations is reported in the report KW2-06-005.

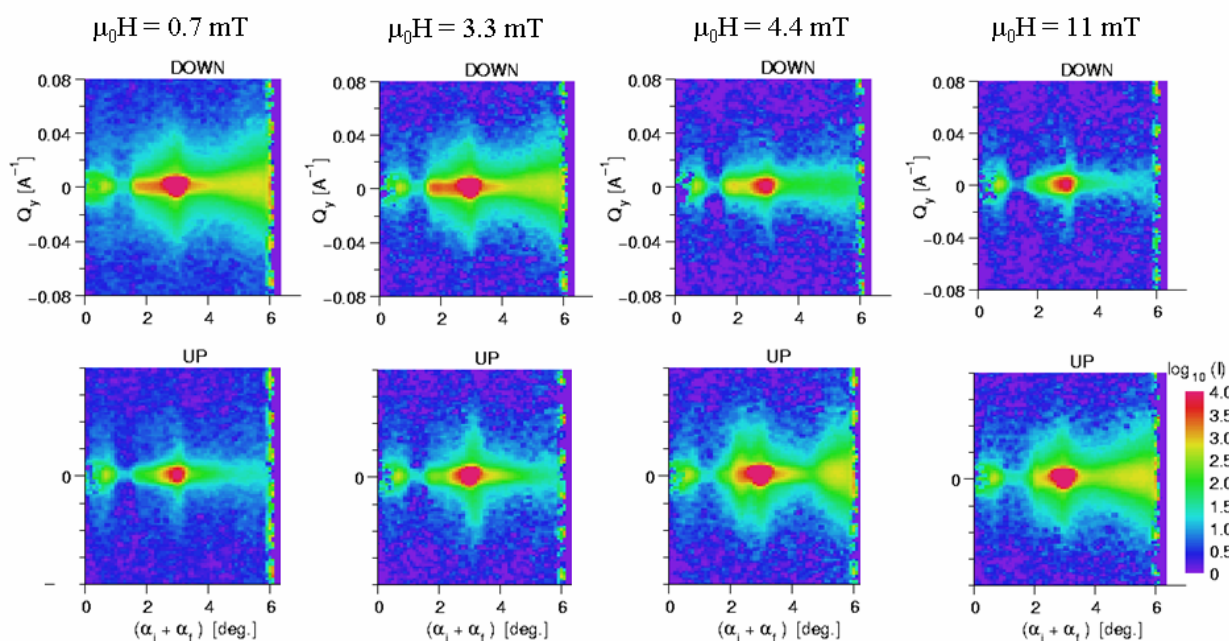


Fig.1: Polarized GISANS measured at $\alpha_i=1.5^\circ$ on a remanent polarizing supermirror at different applied fields $\mu_0 H$. In each case, the same state was measured with incoming spin-down and spin-up neutrons. Exposure time: 13 minutes per field and polarization. Those data can be compared with their unpolarized counterparts (Fig.2 of report KW2-05-003).

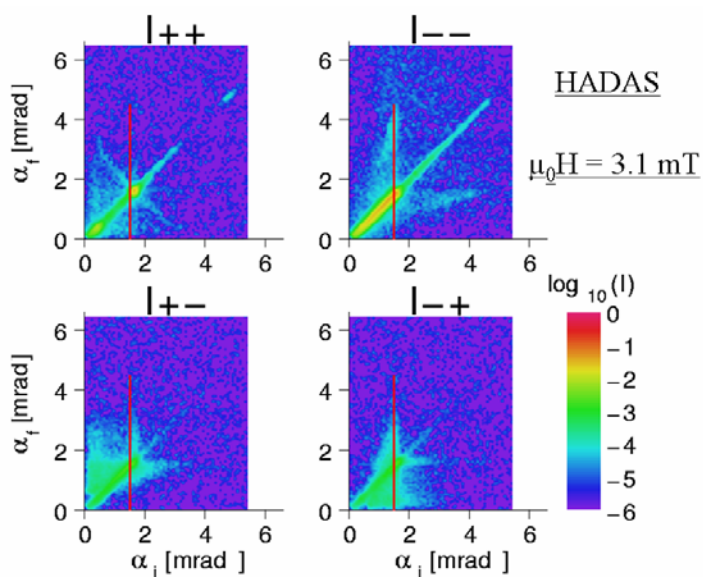


Fig.2: Reflectivity and off-specular scattering from the remanent polarizing supermirror measured on HADAS. This picture is shown in order to explain the GISANS signal measured at $\mu_0 H=3.3$ mT in Fig.1.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-034		
Experiment title:	Self assembly Mechanism of Lysozyme Protein Hydrogels		
Dates of experiment:	10.03-13.03.2006 18.04.2006	Date of report:	04.06.2006
Experimental team: Names			
Dr Aline F. Miller Hui Yan	School of Chemical Engineering and Analytical Science The University of Manchester Sackville Street, PO Box 88, Manchester M60 1QD, UK		
Dr Alberto Saiani Amran Mohammad	School of Materials The University of Manchester Grosvenor Street, Manchester M1 7HS, UK		
Local Contact:	Dr H. Frielinghaus		

Experimental report text body

Proteins have recently attracted considerable attention for their use as building blocks in the construction of novel materials. Many proteins are capable of self-assembling into β -sheet rich fibrils under appropriate conditions via intramolecular or intermolecular hydrogen bonding¹. Such fibrils can further self-organise to form a three-dimensional fibrillar network, i.e. a protein hydrogel, which is able to retain up to 97% water or biological fluid². By varying the amino acid sequence in addition to manipulating environmental conditions, such as sample concentration, pH or ionic strength, novel protein-based materials with desirable properties are beginning to be engineered³.

In order to gain an insight into fibril formation and the gelation mechanism, hen egg white lysozyme (HEWL) has been used as a model protein. Phase diagrams have been mapped out and thermal and mechanical behavior of these systems has been under investigation using micro-differential scanning calorimetry (microDSC) and rheology respectively. Here we focussed on elucidating the structure of lysozyme hydrogels formed under reductive conditions (breaking di-sulphide bridges) as a function of protein and reductant concentration and temperature using SANS. Samples were prepared by dissolving the desired quantity of protein in D₂O, adding 20 or 50 mM of the reductant dithiothreitol (DTT) and heating the system to 90 °C. Above the critical gel concentration of 5 mg ml⁻¹ thermo reversible, transparent hydrogels formed upon cooling.

Typical scattering curves for four different protein concentrations (10, 14.3, 42.9 and 57.2 mg ml⁻¹) with 20 mM DTT at 25 °C are shown in Figure 1. A maximum in scattering was obtained for each sample and its position shifted to higher q values with increasing concentration. An estimated value of the average mesh size, d , was obtained from the position of the peak maximum, q^* , through the Bragg relation: $d = 2\pi/q^*$.

The values obtained decrease as shown in Figure 2 with increasing protein concentration i.e. a denser network is formed. The narrow shape of the maxima observed also suggests the presence of a regular network with a relatively uniform mesh size. These results are in good agreement with those observed with cryo-SEM.

Scattering curves for all concentrations at 90 °C have also been recorded (results not shown). For the low concentration samples (10 and 14.3 mg ml⁻¹) the maximum in scattering disappeared, suggesting the gel network had melted. The peak remained, however, for the two higher concentrations. Such results are in good agreement with micro DSC measurements, which indicate the gels at high concentration had not melted completely at 90 °C. Samples were also diluted to see if we could observe scattering from individual fibrils. A typical Kratky plot is given in Figure 3 and by fitting the curve with a rod model we obtained an average fibril diameter of ~ 6nm.

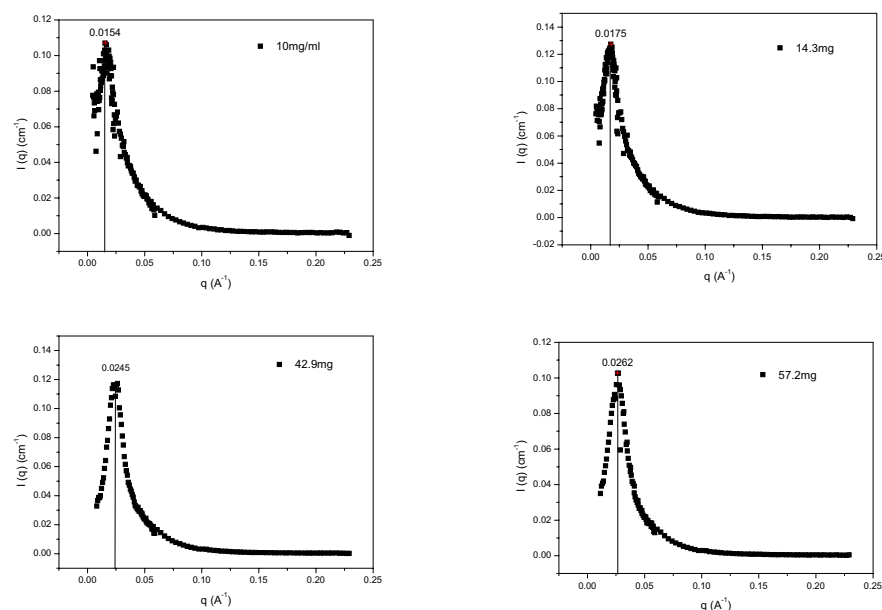


Fig. 1 Scattering curves of HEWL gels at various concentrations measured at 25 °C.

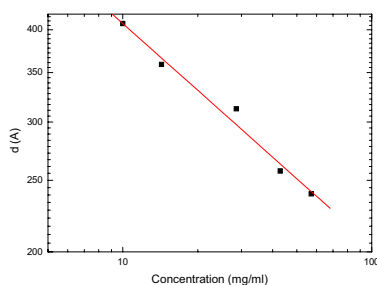


Fig. 2. Estimated mesh size, d , as a function of protein concentration.

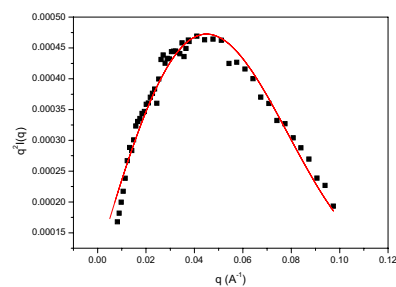


Fig.3 Kratky plot of a diluted gel sample at 25 °C.

The results from our SANS experiments provide evidence of the fibrillar nature of our hydrogel as well as quantitative data on fibril dimension and hydrogel mesh size. We have also been able to identify the key role played by both concentration and temperature.

References

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2. Miller, A.F. *Macromolecular Symposia*, **2005**, 220, 109-114.
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Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-037		
Experiment title:	Structural study of supramolecular aggregates formed by a novel class of contrast agents potentially usable in magnetic resonance imaging techniques		
Dates of experiment:	07/11/2005	Date of report:	15/12/2005
Experimental team:			
Names	Addresses		
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Local Contact:	H. Frielinghaus		

Experimental report text body

Magnetic Resonance Imaging (MRI) is one of the most widely imaging technique used as diagnostic tool in clinical field. Its main advantage is that it allows rapid in vivo acquisition of images, and, under specific conditions, it makes possible imaging at cell resolution. The technique has proven very valuable for the diagnosis of a broad range of pathologic conditions in all parts of the body. Currently, stable Gd^{3+} poly(aminocarboxylate) complexes are widely used as contrast agents in MRI. These agents reduce the relaxation time of water protons present in the tissues, allowing to produce a higher quality (higher contrast) image. Although MRI gives very resolved images, it needs a relatively elevate concentration of contrast agent ($10^{-4} \text{ mol dm}^{-3}$), due to its low sensitivity. To reach the required local concentration, many carriers have been developed such as micelles and vesicles, derivatized with a high number of metallic complexes.

The aim of this research project has been to characterize supramolecular aggregates formed by a new potential blood pool contrast agent $(C_{18}H_{37})_2CONHLys(DTPAGlu)CONH_2^{5-}$, in the following indicated as $(C18)_2DTPAGlu^{5-}$. This molecule, synthesized at the Interuniversity Center for Bioactive Peptides (CIRPeB, Naples) and sketched in figure 1, contains the DTPAGlu chelating agent covalently bound to two C_{18} alkyl chains. The DTPAGlu is considered a very good chelating agent for paramagnetic metal ions (Gd^{3+}) used for applications in magnetic resonance imaging (MRI).

Through SANS measurements performed on both the systems containing $(C18)_2DTPAGlu^{5-}$ and its gadolinium(III) complex $[(C18)_2DTPAGlu(Gd)]^{2-}$, it has been possible to infer the capability of this contrast agents to form micellar and vesicular aggregates, depending on pH and ionic strength conditions.

Figure 2 shows scattering cross sections $d\Sigma/d\Omega$ obtained for binary solutions of $(C18)_2DTPAGlu^{5-}$ ($6.0 \cdot 10^{-4} \text{ mol kg}^{-1}$) at pH=3.0 and pH =4.5. Data obtained show the presence of scattering aggregates in both the systems, although they have very different characteristics.

In fact, $d\Sigma/d\Omega$ values at pH=3 show a power law dependence $d\Sigma/d\Omega \propto q^{-2}$ typical of the presence of bilayers; actually cryo-TEM measurements performed on this system have shown the existence of unilamellar vesicles that, due to the their dimension, may be regarded, in the q range spanned by SANS measurements performed, as randomly oriented infinite planar sheets. If τ represents the thickness of the sheets, in the region where $q\tau \ll 1$ scattering cross sections can be represented in a form analogous to the Guinier equation used to get radius of gyration

$$\ln\left(\frac{d\Sigma}{d\Omega} q^2\right) \cong \ln\left[2\pi S(\Delta\rho)^2 \tau^2\right] - \frac{q^2 \tau^2}{12} \quad (1)$$

where S is the area of sheet per unit volume of sample, whereas $\Delta\rho$ is the scattering length density difference

between the sheet and the solvent. Thus, by reporting $\ln(q^2 d\Sigma/d\Omega)$ vs. q^2 a straight plot with a slope $\tau^2/12$ should be obtained, allowing to determine the thickness of the vesicular double layer.

On the other hand, the pH growth from 3.0 to 4.5 leads to the destruction of the vesicular structure; in this case the power law found in SANS spectra, $d\Sigma/d\Omega \propto q^{-1}$, is characteristic of cylindrical aggregates. The presence of such transition can probably be attributed to the repulsion among the polar heads of DTPAGlu units: when pH is increased, carboxylic groups of DTPAGlu heads are deprotonated and repulsions start to become strong. This picture agrees with SANS measurements executed on $[(C18)_2DTPAGlu(Gd)]^{2-}$ solutions: such measurements have shown the presence of vesicles at pH=3.0 that still exist if pH is increased at 4.5. Gd-complexed DTPAGlu units have a smaller charge (-2); as result of that, the repulsions among polar heads are smaller if compared to those of DTPAGlu units. Effect of ionic strength has also been analyzed: the presence of NaCl in the system partially shields repulsions among polar heads. Indeed aqueous solutions of $[(C18)_2DTPAGlu(Gd)]^{2-}$ in the presence of NaCl, show vesicular aggregates even at physiological pH values (7.4).

Table 1 reports the values of τ obtained through eq. (1) for the systems analyzed, and the values of the radius R of cylindrical aggregates obtained by using the Guinier approximation of a cylinder form factor

$$\ln\left(\frac{d\Sigma}{d\Omega} q\right) \cong \ln\left[(\Delta\rho)^2 \phi_{cyl} (1-\phi_{cyl}) \pi^2 R^2\right] - q^2 \frac{R^2}{4} \quad (2)$$

where ϕ_{cyl} is the volume fraction of cylindrical aggregates. Actually the length of the cylinders cannot be extracted from the scattering data in the accessible range of the scattering vector q as indicated by the missing of the Guinier region at small q .

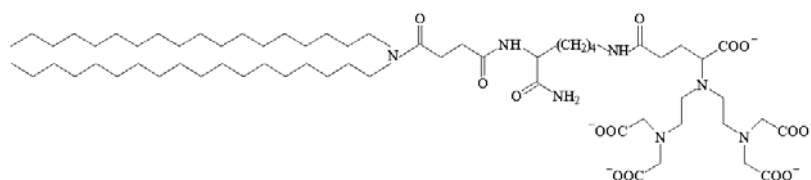


Figure 1 – Molecular structure of the $(C18)_2DTPAGlu^{5-}$ unimer.

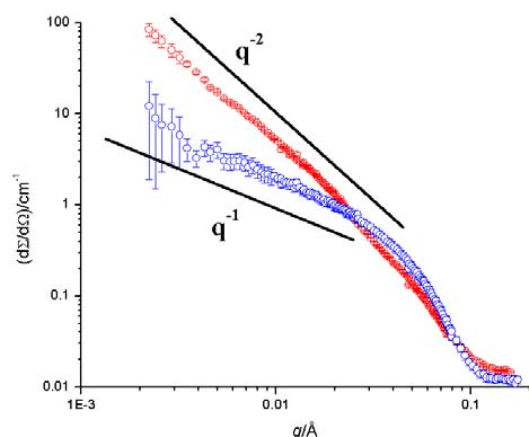


Figure 2 – Scattering cross sections obtained at 25°C for $(C18)_2DTPAGlu^{5-}$ ($6.0 \cdot 10^{-4}$ mol kg^{-1}) at pH 3.0 (—) and 4.5 (—) in D_2O .

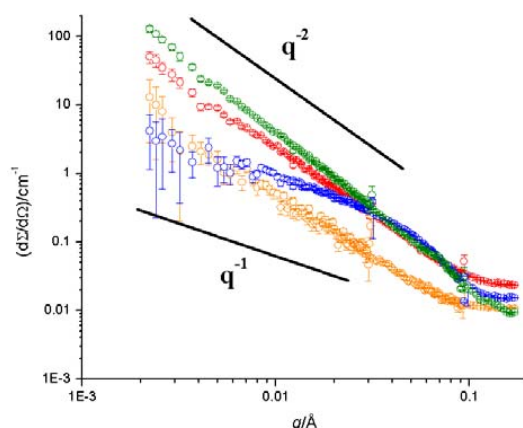


Figure 3 – Scattering cross sections obtained at 25°C for $[(C18)_2DTPAGlu(Gd)]^{2-}$ ($4.1 \cdot 10^{-4}$ mol kg^{-1}) at pH 3.0 (—), 4.5 (—), and 7.4 (—) in D_2O , and at pH 7.4 (—) in NaCl 0.9% and D_2O .

	$(C18)_2DTPAGlu^{5-}$		$[(C18)_2DTPAGlu(Gd)]^{2-}$			
	pH 3.0	pH 4.5	pH 3.0	pH 4.5	pH 7.4	pH 7.4 + NaCl
$\tau/\text{\AA}$	47 ± 5	—	51 ± 6	53 ± 8	—	53 ± 4
$R/\text{\AA}$	—	38 ± 4	—	—	35 ± 3	—

Table 1 – Values obtained from SANS data relative to the vesicular double layer thickness and the cylindrical radius of micelles.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-039		
Experiment title:	Test of the small detector		
Dates of experiment:	14.12.2005	Date of report:	07.03.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus	Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

<u>Experimental report text body</u>	Test of the small detector
The new small detector is mounted at the KWS-2 for testing purposes. It is freely movable in front of the large area detector, but with a much higher resolution ($0.5 \times 0.5 \text{ mm}^2$) in order to resolve much tinier structures than the large detector does ($5 \times 5 \text{ mm}^2$). Finally in Munich, the new small detector will be operative at KWS-1 (and KWS-2) in order to obtain the following options: (a) In the center, close to the primary beam, one obtains much smaller scattering vectors which will be comparable to those of KWS-3 ($Q \approx 10^{-4} \text{ \AA}^{-1}$). Here, a small collimation aperture is chosen. Lenses will improve the intensity and resolution. (b) Off the center, the peak width of sharp Bragg peaks can be resolved. A small collimation aperture is needed and neutron lenses are helpful. Additionally, a very good wavelength resolution ($\sim 1\%$) is needed, which will be obtained in a time-of-flight mode with a chopper. (c) In the grazing incidence (GI) SANS mode the scattered intensity is to be observed as well. Close to the specular reflex the wavelength resolution can be relaxed ($\sim 10\%$), whereas at larger scattering vectors the wavelength must be defined more precisely ($\sim 1\%$). For the GISANS mode lenses might help to increase the intensity, but the gain is due to only one dimension, which is certainly less than for the conventional SANS mode. Two tests were performed in the conventional SANS geometry (as described by a and b). The first test of the small detector aimed at the primary beam, in order to get an idea about the minimal scattering vector possible. The second test was done with a diblock copolymer in a lamellar, ordered state. Due to the random orientation of the crystallites the powder-like sample showed a Debye-Scherrer ring. This ring was measured with the large detector and the small detector. The collimation aperture at 20m distance was opened to $3 \times 3 \text{ mm}^2$. The sample aperture was $1 \times 1 \text{ mm}^2$. At a detector distance of 20m, the primary beam was measured by the small detector. The primary beam had a FWHM size of 8x8 pixels. Therefore the minimal possible scattering vector is $4 \text{ pixels} \times 0.5 \text{ mm} / 20000 \text{ mm} = 1 \times 10^{-4} \text{ \AA}^{-1}$. Since the primary beam simply looks tiny no figures are depicted.	

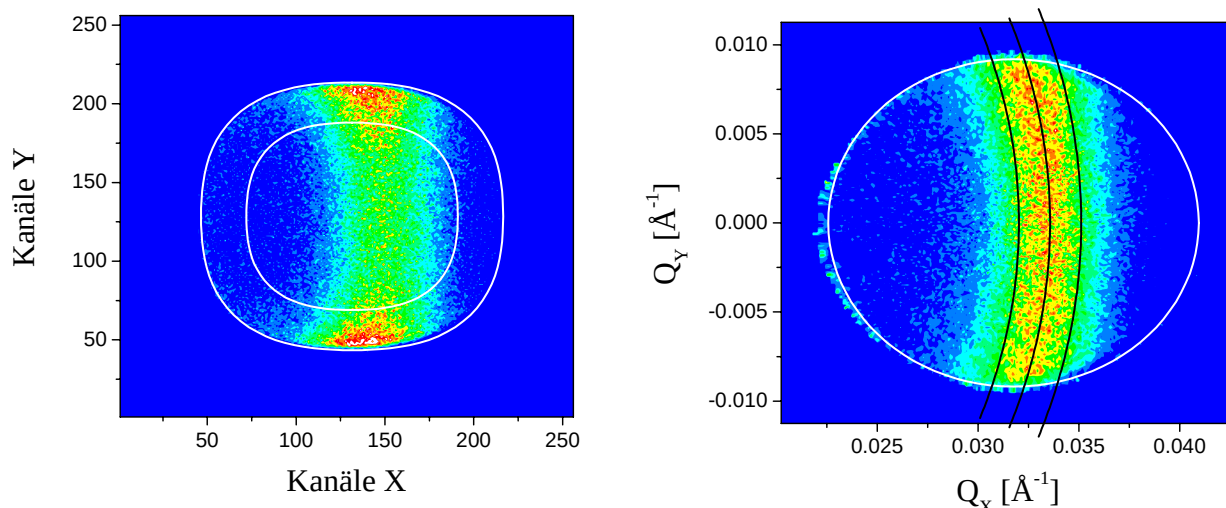


Figure 1: Section of a Debye-Scherrer ring measured with the new small detector. On the left side, the rawdata as obtained is shown. The detector has some square shaped distortions and furthermore the outer regions are compressed to a smaller area in the pixel memory. Therefore, more counts are obtained in the outer regions compared to the centre. The pixels can be mapped quite well on a non-distorted pixel-space as shown on the right hand side. Furthermore, the intensities are corrected by a sensitivity measurement. The final picture shows a section of a Debye-Scherrer ring with a reasonable intensity distribution.

The second test was made with the Debye-Scherrer ring of a diblock copolymer. The small detector was positioned on the right center of the ring as visualized by Figure 1. The obtained rawdata shows two defects of the small detector: (i) The pixels are mapped in a distorted way. Circles appear square like, and the outer regions of the detector are compressed to less pixels than the inner part. (ii) The measured intensity in the compressed outer part appears higher due to this mapping.

The intensity can be corrected by a sensitivity measurement. An incoherent Plexiglas sample scatters homogenously in all directions. The recorded intensity reflects all imperfections intensity-wise. The mapping of the pixels was followed by measuring a tiny primary beam. By moving the primary beam from the center to the outer parts (horizontally, vertically, and diagonally) the distortions of the mapping can be measured. A harmonic distortion with 4 maxima (octopole) was assumed to describe the real distortion. As observed by the corrected Debye-Scherrer ring the corrections seem to work very well. A refined measurement with a pinhole grid is about to show more details.

When comparing the intensity in the azimuthally averaged form between the large detector and the small detector, the small detector yields a 10 times higher density of data points. Unfortunately, the resolution of both measured curves is exactly the same. For finite scattering vectors ($Q = 0.033 \text{ \AA}^{-1}$) the resolution is strongly dependent on the wavelength distribution (10%), which could not be varied. Only by a chopper, a time of flight mode would allow to reduce the wavelength distribution to 1%. For the newly upgraded instruments in Munich this chopper is highly desirable.

Thus the new small, high resolution detector is successfully tested. In the ultra small angle mode lowest scattering vectors of $1 \times 10^{-4} \text{ \AA}^{-1}$ are expected. In the high resolution mode at finite scattering angles a better wavelength resolution is required. The corrections of the distortions of the detector electronics seem to be promising. Thus, the full area of the small detector will be useful to collect as much data as possible. This correction can be transferred to other instruments using the same detector, namely KWS-3, MARIA and TREFF.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-040, KW2-05-050, KW2-06-001, KW2-06-006, KW2-06-013		
Experiment title:	Confinement Effects of Triblock Copolymers in Bicontinuous Microemulsions – Part I, II, III, IV, V		
Dates of experiment:	04 - 05.12.2005 28 - 29.01.2006 18 - 20.02.2006 23 - 25.03.2006 08 - 09.04.2006 30.04.2006	Date of report:	10.05.2006
Experimental team: Names	Addresses		
Simona Maccarrone Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Microemulsions are thermodynamically stable and macroscopically homogeneous mixtures of two otherwise non-miscible components like oil and water, which are mediated by a third component, the surfactant. Microscopically oil and water form domains, the surfaces of which are covered by the amphiphile. For equal volumes of oil and water a minimum amount of surfactant is needed to form a one-phase bicontinuous microemulsion. This amount is a measure for the efficiency of the surfactant.

When adding amphiphilic diblock copolymers to the microemulsion, this macro surfactant molecule is anchored in the surfactant membrane, and the two different blocks are situated in their pleasant environment (Endo). Furthermore, the bending rigidity of the surfactant membrane is increased. This result explains the empirically found polymer boosting effect, which describes a drastic enhancement of the surfactant efficiency. Stiffer membranes allow the formation of larger domains with a better surface to volume ratio. Theories (Lipowsky) agree well with these first studies.

In our latest studies we studied diblock copolymers in microemulsions rendering the domain size d comparable to the polymer size (R_g). At relatively large d/R_g the confinement is weak, and the sensitivity of the polymer boosting effect is unchanged. With increasing confinement (d/R_g closer to 1) the sensitivity is only slightly enhanced, and finally a strongly reversed behaviour (anti-boosting) is observed. The behaviour at medium confinement shows a much lower sensitivity compared with the theory of Auth. This enhancement would have been very interesting for applications, while the reversed behaviour could be an explanation how red blood particles could sneak into small vessels.

The new polymer we studied is an amphiphilic triblock copolymer. This polymer has a hydrophilic mid-block of poly-ethylene oxide and two hydrophobic ends of relatively low molar mass. This polymer is able to anchor

at two points in the membrane (bridging). Choosing different domain d sizes compared to the polymer size (R_g) the bridging should change from connecting neighboured points (quite high d/R_g) to connecting also opposite membrane points (medium d/R_g). At medium confinement an enhanced boosting should be visible. At high confinement (low d/R_g) the anchoring should not play any role anymore and an anti-boosting should be observed.

The domain size was practically changed by the use of different oils (tetradecane, dodecane, decane, octane, hexane) as well as different surfactants were used to span a very wide range of confinement. Three polymer compositions δ were combined with three surfactant compositions γ around the critical point.

The strategy of the experiments was to combine macroscopic observations of the phase behaviour with microscopic measurements of the structure by small angle neutron scattering (SANS). Then both results will be compared on the basis of a common theoretical background. The Helfrich theory describes the elastic properties of the surfactant membrane to be dominating. The bending rigidity κ is the modulus of the mean curvature while the saddle splay modulus $\bar{\kappa}$ is connected with the Gaussian curvature. By SANS the structure of a microemulsion is studied, which can be characterized by the domain spacing d and the correlation length ξ . The Gaussian random field theory connects these two parameters with the bending rigidity κ . The phase diagram measurements can be connected with the modulus $\bar{\kappa}$. At the emulsification failure point (fish tail point, FTP) the spatially renormalized modulus $\bar{\kappa}_R$ is approximately zero, and changes of the surfactant content at the FTP give insight about relative changes of $\bar{\kappa}$ with changing polymer content. Thus two types of measurements can be compared on the basis of the theoretical concept of Helfrich.

Experimentally, we have found three configurational transitions as expected at $d/R_g \approx 2, 5$ and 8 (see figure 1). At high confinement ($d/R_g < 2$) from the diblocks already observed reversed behaviour is found. Then at intermediate confinement ($2 < d/R_g < 5$) an enhanced polymer boosting effect is found. In the next region ($5 < d/R_g < 8$) the chances of bridging slowly fades away, and finally at very low confinement ($d/R_g > 8$) the state is reached where only neighbouring points of the membrane are connected by the polymer. The observed regions are accompanied by other signals of the sensitivity of $\bar{\kappa}$ (not shown here).

All in all, the transition from medium confinement with enhanced boosting to low confinement with an anti-boosting might be very useful in applications. In processes the enhanced emulsification ability might be used in concert with high concentrations, while a separation of oil and water might be of interest after the cleaning process. So here we have found an intelligent polymer additive which reacts on the environment or process stage.

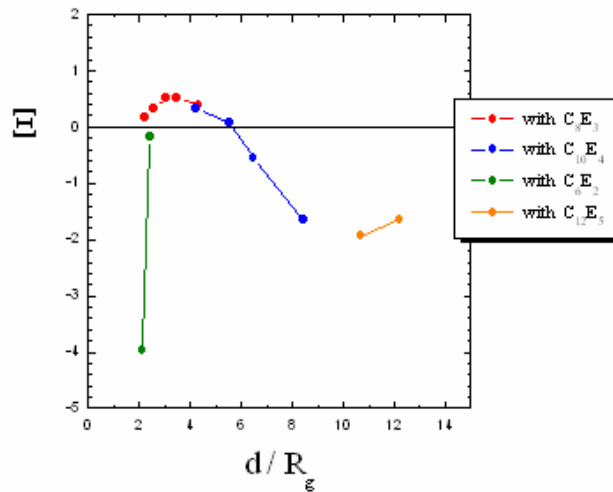


Figure 1: The sensitivity Ξ of the triblock copolymer effect on the bending rigidity as a function of the reciprocal confinement (d/R_g). The different coloured points are obtained by SANS measurements sorted by surfactants used.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-041		
Experiment title:	Polarized neutron measurements of Co nanoparticles in solution		
Dates of experiment:	16.12.2005 - 18.12.2005	Date of report:	20.01.2006
Experimental team: Names	Addresses		
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Local Contact:	A. Radulescu		

Experimental report text body

This experiment was the first part of the long-time proposal “Polarized neutron measurements of Co nanoparticles in solution” (KW2-05-041). We performed *non-polarized* small-angle neutron scattering on dodecanethiol-stabilized cobalt nanoparticles in d_8 -toluene as preliminary experiment in order to be successfully able to consequently carry out polarized neutrons experiment.

The aim of the experiment was twofold: First, to obtain the scattering cross-section of Co nanoparticles in absolute units to thus be able to estimate the time needed to perform the polarized neutrons measurements. The second aim was to completely characterize the samples prepared. The Co-nanoparticles are originally synthesized by reducing Co^{2+} in a microemulsion medium. To stabilize the particles formed against instantaneous oxidation it is necessary to add dodecanethiol ($\text{C}_{12}\text{H}_{26}\text{S}$) to the microemulsion -as ligand that binds on the particle surface- prior to particle separation. Afterwards the Co-nanoparticles are precipitated by addition of a non-solvent (for the thiol-chain) to the microemulsion followed by centrifugation/filtration and re-dispersion steps to wash the particles free of any microemulsion residues. Finally toluol, which is used as good solvent for the thiol-chains, is evaporated and replaced by d_8 -toluene. In this way dissolved thiol might additionally be present in the Co-nanoparticle dispersions and it is difficult to determine the accurate particle concentration. Therefore, we wanted to determine particle size and polydispersity as well as concentration.

To explore the possible concentration range, we investigated two samples (S60 and S61), whereby S61 was approximately 3 times more concentrated than S60 and also of higher purity. All measurements were performed at ambient conditions at a wavelength of $4.5\text{\AA}$. During our beam time, we were only able to measure S60 and S61 within a Q-range of $0.02\text{\AA}^{-1} - 0.15\text{\AA}^{-1}$ (corresponding to detector distances 2m and 8m, respectively) and S60 in the Q-range of $0.006\text{\AA}^{-1} - 0.05\text{\AA}^{-1}$. Additionally planed experiments could not be performed, because of a velocity selector problem occurring at the third day. Using a collimation distance of 4m at a detector distance of 2m increased significantly the number of incoming neutrons and thus decreased the measuring time by a factor of about 3. Quartz cells of 1mm were used as sample containers.

The measured scattering curve of sample S60 is presented in Fig.1 together with a simulation in absolute units. The particles display in a shell contrast due to the bound thiol (mono)layer (see inset). We attribute the upper part of the scattering curve to the scattering from Co nanoparticles which interferes at high Q with the scattering

from smaller particles, which might stem from aggregates of protonated dodecanethiol molecules in d_8 -toluene. These aggregates are significantly smaller (form factor minimum not seen up to $Q=0.15 \text{ \AA}^{-1}$) than the Co-nanoparticles, but display a better contrast due to the larger difference in scattering length density between protonated dodecanethiol and d_8 -toluene compared to cobalt and d_8 -toluene. Therefore only small amounts of thiol aggregates can contribute already significantly to the scattering curve. The blue curve is simulated for spherical Co nanoparticles in d_8 -toluene in core – shell contrast with a mean size of 9nm and polydispersity of 30%. The green curve shows the simulated contribution from small particles of protonated dodecanethiol with a mean size of 3nm and polydispersity of 14%. The model assumes tabulated values for scattering length densities of all materials in the sample.

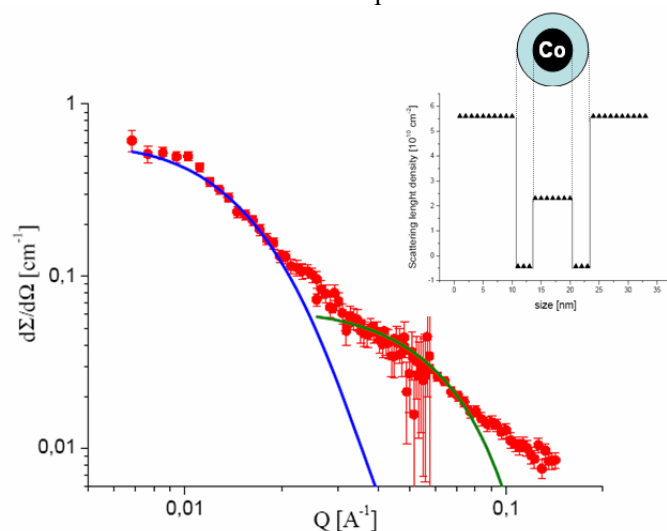


Fig.1.: Cobalt nanoparticles dissolved in d_8 -toluene data and simulation. Inset: scattering length density profile of these particles assumed in simulation (blue curve).

In order to determine the increase in scattering intensity by using polarized neutrons the following simulation was performed: Due to the magnetic properties of cobalt the scattering length density increases under saturation conditions for neutrons polarized along the magnetic moments of cobalt (so-called “spin up” state of neutrons). This leads to an increase of the scattering intensity by a factor of 100 (compared with non – polarized neutron scattering) as shown in Fig.2.

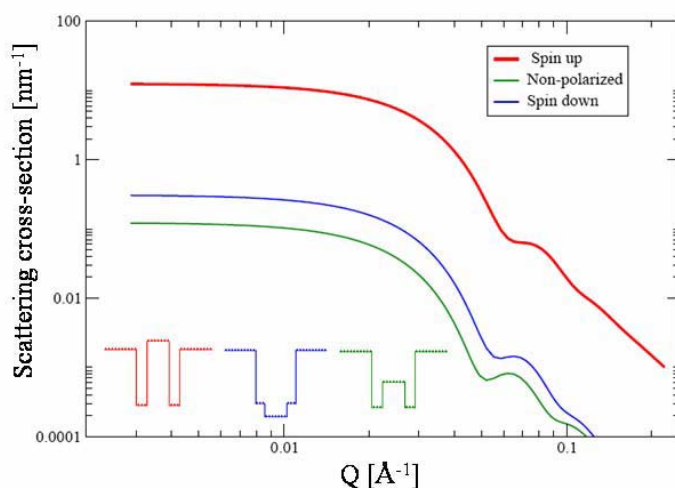


Fig.2.: Simulations of polarized small angle neutron scattering from Co nanoparticles in d_8 -toluene. Inset: scattering density profile for spin up polarization, spin down and for unpolarized neutrons.

Based on the polarized neutron simulations and results from earlier reported SQUID measurements, we intend to use a polarized neutron setup for our next beam time at KWS-2. The measurements will be performed at room temperature within a permanent magnetic field of 0.5 T. To additionally increase the scattering intensity we would like to use 2mm quartz cells and to also measure an as high as possible concentrated particle dispersion.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-043		
Experiment title:	Small-angle neutron scattering of $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ Heusler films		
Dates of experiment:	6.12.2005-9.12.2005	Date of report:	16.12.2005
Experimental team: Names	Addresses		
Dr. Diana Rata	IFF/FZJ		
Dr. Emmanuel Kentzinger	IFF/FZJ		
Dr. Aurel Radulescu	IFF/FZJ		
Dr. Daniel Buergler	IFF/FZJ		
Local Contact:	Dr. Henrich Frielinghaus, Dr. Aurel Radulescu		

Experimental report text body

We performed small-angle neutron scattering experiments on KWS-2 in order to investigate the magnetic structure, in particular the magnetic domains, of $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ Heusler alloys thin films.

Previous experiments, *e.g.* magnetization *versus* temperature and x-ray magnetic circular dichroism, revealed a reduced magnetic moment compared to the theoretical bulk value. This could be due to atomic disorder (*i.e.* random distribution of Fe, Cr, and Al atoms in the cubic unit cell), which is an intrinsic characteristic of the Heusler compounds. A random distribution (fluctuations) of small magnetic domains could also give a strong decrease of the magnetic moments and of the spin polarization compared to the expected values. Neutron scattering is therefore a method of choice to get access to the domain structure throughout the volume of the Heusler films.

First test measurements were done on a 300 nm thick $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ film grown by magnetron sputtering on SiO_2 substrate. The Heusler films are ferromagnetic with Curie temperatures up to 600 K and magnetically very soft. Therefore, we measured at room temperature and small magnetic fields with unpolarized neutrons. We performed SANS and GISANS measurements at three different sample-to-detector distances, *e.g.* D2, D8, D20, in order to cover the whole Q range accessible with a neutron wavelength of 6 Å.

The most striking feature is the scattering at high Q values, which is characteristic for scattering from ~5 nm diameter clusters in a homogeneous matrix. In Fig. 1, we show the data obtained at C4-D2 for two different magnetic fields: saturating (11 mT) and coercive (6 mT) fields, respectively. This result is encouraging for further investigation.

In order to check whether this scattering is of magnetic origin, we would like to perform scattering of polarized neutrons. If the contrast between clusters and matrix is due to different net magnetizations, different intensities should be observed for + and – neutrons.

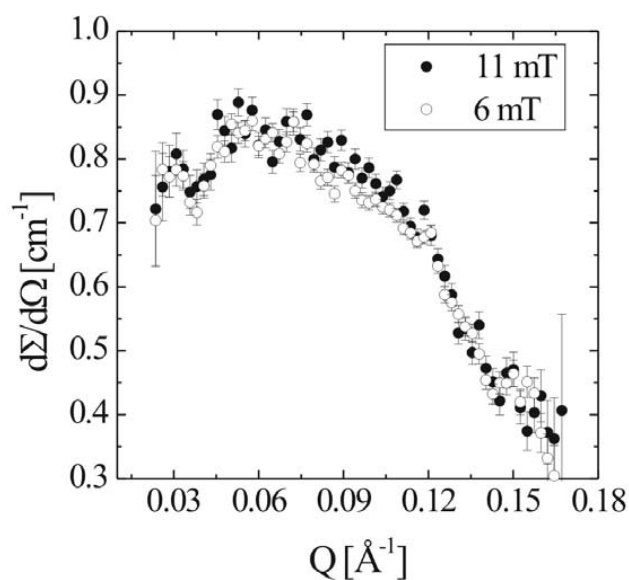


Figure 1. SANS scattering from a 300 nm thick CCFA film at C4-D2 for 2 different fields.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-05-044		
Experiment title:	Structure modification of the multi-segment PEB-n random copolymer aggregates in solution induced by paraffin waxes		
Dates of experiment:	30.11.05-02.12.05	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.H.Frielinghaus		

Experimental report text body

The self-assembly of poly(co-olefins) in dilute solution has been shown via SANS to yield either plate-like or needle-like micelles-like micelles [1,2]. The resultant supramolecular structures are dependent upon the copolymer architecture. The crystalline-amorphous diblock co-polymers yield self-assembled hairy plates while the corresponding random co-polymers yield one-dimensional needle shaped aggregates. The PEB-n random copolymers (n - the number of ethyl sides per 100 backbone carbons) show selectivity in their wax crystal modification capacities depending on the ethylene content of the backbone. This behavior relates to the graded ethylene content of PEB-n copolymers that leads to different self-assembling temperatures: the lower n, the higher the self-assembling temperature [2]. All PEB-n copolymers self-assemble in open 1-d structures. This conclusion has stimulated further structural studies of multiblock copolymers in solution where blocks represent poly(ethylene-butene) random copolymers (PEB-n) showing graded ethylene contents and thus, different crystallization degrees. Recently [3] conventional and focusing SANS studies of self-assembling in decane solution of a triblock and tetrablock PEB-n copolymers have been performed. The structural results complimented by microscopy observations concluded that these materials form in solution core-shell structures showing a 1D overall aspect which associate and give raise to occurrence of large scale spherulitic-like soft aggregates with sizes within the micrometric range. The conventional SANS investigations have shown that these multiblock copolymers modify the wax crystals morphology from big compact crystals with sizes of hundreds of micrometers as in the case of pure wax solution into 2-dimensional thin aggregates. In the present study we investigated the influence of the wax addition to the structure of the polymer aggregates. We performed at KWS2 instrument systematic SANS measurement of different combinations of waxes and multiblock copolymers for the contrast condition allowing the polymer visible. The solutions have been scanned over a very wide temperature range between the single coil regime and the aggregation regime, at temperatures well below 0°C. The influence of the wax addition to the structure of the polymer aggregates

could be noticed at temperatures below the wax crystallization point, the lower the low wax concentration is. Fig.1 and 2 show the scattering patterns of the two multiblock copolymers investigated, the triblock PEB-6.5/8.9/10.1 and the tetrablock PEB-2.6/6.0/10.9/13.2 copolymers in parallel for the polymers alone in solution and mixed with C24 or C36 waxes in common solutions. The modifications of the scattering patterns when waxes are added are obvious. The overall morphology of the polymer aggregates which is characterized by the scattering at low Q does not change and seems to be that of 1-dimensional objects. Nevertheless, at low Q the level of the scattered intensity increases strongly when the wax is added which may lead to a conclusion that changes in either the contrast or the size of aggregates take place. The most evident qualitative changes occur at intermediate and high Q and prove that modification of the intimate structure of the 1D aggregates appear when wax starts to crystallize and interacts with the already formed polymer objects. We may conclude that a modification of the proposed core-shell morphology of the 1D aggregates takes place. A model interpretation of the experimental data is in progress.

References: [1] D.Schwahn et al., Macromolecules 35, 861, 2002; [2] A.Radulescu et al. J.Pol.Sci. B Pol.Phys. 42, 3113, 2004; [3] experimental reports KW2-05-002;KW3-05-001 FRJ-2 Jülich.

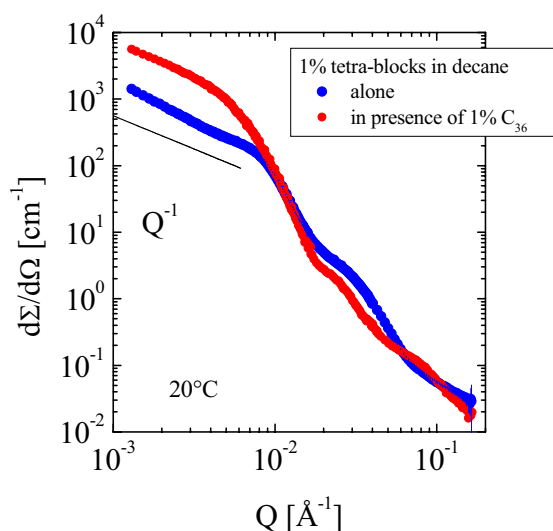


Fig.1 – The tetra-block copolymer scattering patterns when is alone and mixed with the C36 wax in decane.

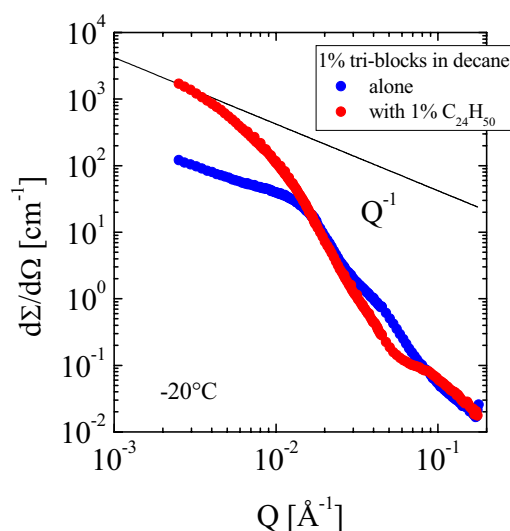


Fig.2 – The tri-block copolymer scattering patterns when is alone and mixed with the C24 wax in decane.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-045		
Experiment title:	Study of solutions of chitosan and poly(vinyl pyrrolidone) in the presence of anionic surfactants		
Dates of experiment:	08/12/2005	Date of report:	15/12/2005
Experimental team: Names	Addresses		
Gaetano Mangiapia	IFF – Neutronenstreuung, Forschungszentrum Jülich GmbH, D-52425 Jülich Tel. +49 2461 61 6048 (g.mangiapia@fz-juelich.de)		
Local Contact:	H. Frielinghaus		

Experimental report text body

Chitosan [CHT] is a polymer that is currently receiving a great deal of interest for medical and pharmaceutical applications, because of its non-toxicity, the high biodegradability and the capability to form hydrogels potentially usable as carrier for drug delivery applications. Furthermore this substance can be obtained in large quantities and in a very cheaply way, through the deacetylation of an alkaline solution of chitin, a natural compound extractable from crab shell.

The addition of hydrophilic polymers such as poly(vinyl pyrrolidone) [PVP], allow obtaining gels with better features compared to CHT alone. These include reduced irritation, improved film quality, improved flexibility, and enhanced drug dissolution. Blends of CHT with different hydrophilic polymers could thus be promising candidates for formulation in oral mucosal delivery systems.

Our research program is currently devoted to explore the possibility to use CHT/PVP hydrogels as drug delivery systems. The addition of a surfactant, through micelles formation, should allow creating hydrophobic domains whose extension could be modulated at will, useful for embedding lipophilic molecules. Previous SANS investigations on chemical hydrogels formed by CHT in the presence and absence of PVP have been performed (proposal nr. KW2-05-020). Effect of sodium decylsulfate [C10OS] in the gel matrix has also been analyzed, and in all cases no or weak interaction has been observed between the surfactant and the polymer matrix.

In order to get information on eventual interactions occurring among CHT, PVP and C10OS in solution, SANS measurements on the relative systems have been performed. Actually CHT is not soluble in water because of the neutral pH value of H₂O; by increasing the acidity of the system, aminic groups are protonated, and the solubility of the polymer grows up. SANS measurements of PVP in D₂O, in the presence and absence of C10OS have thus been performed.

Figure 1 reports scattering cross sections for PVA (1% wt) in D₂O in the absence and the presence of fully deuterated C10OS [DC10OS]. The inspection of the figure reveals a quite different conformation of PVP, depending on the presence of the surfactant. In the absence of C10OS, PVP can be described in terms of a Gaussian coil conformation, and the Debye equation can be fit to the experimental scattering cross sections $d\Sigma/d\Omega$, obtaining the gyration radius of the polymer R_g (see table 1)

$$\frac{d\Sigma}{d\Omega}(q) \propto \frac{\exp(-q^2 R_g^2) + q^2 R_g^2 - 1}{q^4 R_g^4} \quad (1)$$

On the other hand, conformation of PVP changes in the presence of C10OS. For this system, reported in figure 1, deuterated C10OS in heavy water was used in order to make very small the contrast between the solvent and the surfactant. Finally, to gain structural information on the system, measurements on PVP – C10OS – D₂O

ternary solutions have been performed. In figure 2 is reported one of the spectra obtained; for comparison scattering data collected for the system C10OS–D₂O at the same concentration of the surfactant are also reported. As it is possible to infer from the figure, the existence of a single broad maximum indicates the presence of aggregates with significant intercorrelations. The position of the maximum in $d\Sigma/d\Omega$ occurs at different values of the scattering vector modulus q , indicating different correlation distances in the two systems, i.e. the presence of micellar clusters in the ternary system bound onto the polymeric chains.

All data shown in figure 2 have also been analyzed quantitatively. Table 1 reports values obtained for C10OS micelles in D₂O: micelles have been modeled as charged prolate ellipsoids. From the fitting it has been possible to extract the micellar aggregation number N_{agg} , the actual charge z , the major and minor semiaxis of the hydrophobic core a and b , and the thickness of the hydrophilic shell δ . By neglecting scattering from PVP chains, it has also been possible to have information on the clusters, reported in table 1; in the analysis clusters have been treated as charged spherical objects ($a=b$), and the volume fraction of the polymer penetrated inside the micellar hydrophilic shell ϕ_{PVP} has been evaluated.

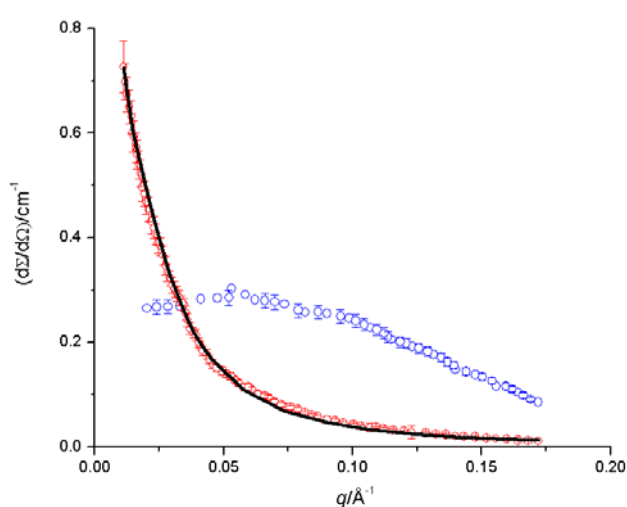


Figure 1 – Scattering cross sections obtained at 25°C for PVP (1%) in the absence (—) and in the presence (—) of DC10OS (0.08 mol kg⁻¹) in D₂O. For the first system, curve obtained from the fitting of the model described in the text is also reported.

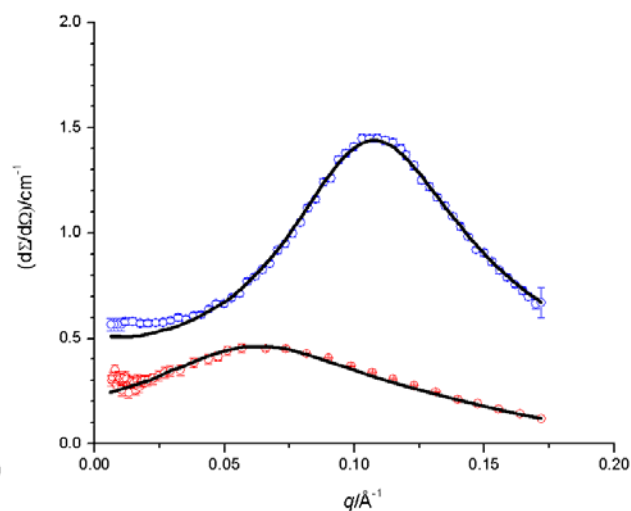


Figure 2 – Scattering cross sections obtained at 25°C for C10OS (0.08 mol kg⁻¹) in the absence (—) and in the presence (—) of PVP (1%) in D₂O. Curves obtained from the fitting of the model described in the text are also reported.

	$R_g/\text{\AA}$	N_{agg}	z	$a/\text{\AA}$	$b/\text{\AA}$	$\delta/\text{\AA}$	ϕ_{PVP}
PVP	62 ± 3	—	—	—	—	—	—
C10OS	—	50 ± 4	-25 ± 3	17.1 ± 0.4	14.1 ± 0.5	4.5 ± 0.9	—
PVP – C10OS	—	30 ± 2	-20 ± 2	12.5 ± 0.5	12.5 ± 0.5	3.7 ± 0.4	0.25 ± 0.06

Table 1 – Structural parameters obtained for PVP, C10OS, and PVP/C10OS solutions in D₂O. In all the systems containing C10OS, the concentration of surfactant is 0.08 mol kg⁻¹.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-05-048		
Experiment title:	Small-angle neutron scattering of $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ Heusler films		
Dates of experiment:	15.03.2006 – 17.03.2006	Date of report:	31.05.2006
Experimental team: Names	Addresses		
Dr. Diana Rata	Institut für Festkörperforschung, Forschungszentrum Jülich		
Dr. Emmanuel Kentzinger	Institut für Festkörperforschung, Forschungszentrum Jülich		
Dr. Aurel Radulescu	Institut für Festkörperforschung, Forschungszentrum Jülich		
Dr. Daniel Buergler	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Dr. Henrich Frielinghaus, Dr. Aurel Radulescu		

Experimental report text body

We performed small-angle neutron scattering experiments on KWS-2 in order to investigate the magnetic structure, in particular the magnetic domains, of $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ Heusler alloys thin films.

Previous experiments, *e.g.* magnetization *versus* temperature and x-ray magnetic circular dichroism, revealed a reduced magnetic moment compared to the theoretical bulk value. This could be due to atomic disorder (*i.e.* random distribution of Fe, Cr, and Al atoms in the cubic unit cell), which is an intrinsic characteristic of the Heusler compounds. A random distribution (fluctuations) of small magnetic domains could also contribute to the reduction of the magnetic moment and of the spin polarization, which is predicted to be 100% [1].

Neutron scattering is therefore the method of choice to get access to the domain structure throughout the volume of the Heusler films.

Small-angle neutron scattering experiments were done on 300 nm thick $\text{Co}_2\text{Cr}_{0.6}\text{Fe}_{0.4}\text{Al}$ films grown by magnetron sputtering on SiO_2 substrate at room temperature. The Heusler films are ferromagnetic with Curie temperatures up to 600 K and magnetically very soft [2]. Therefore, we measured at room temperature and small magnetic fields with unpolarized neutrons. We performed SANS measurements at two different sample-to-detector distances, *e.g.* D2 and D4, in order to cover the whole Q range accessible with a neutron wavelength of 4.5 Å.

Two interesting effects were observed in this experiment. Firstly, a clear magnetic field dependence of the scattering intensity was detected. In Figure 1, we show the data obtained at C8-D2 for three different magnetic fields: saturating (11 mT), coercive (6 mT) fields and zero field, respectively.

Secondly, a striking feature is the scattering at high Q values, which is characteristic for scattering from approximately 6 nm diameter clusters in a homogeneous matrix. Further investigation, using polarized neutrons, is needed in order to explain the origin of these effects. Small magnetic domains having a different net magnetization than the host matrix should give different intensities for + and – neutrons.

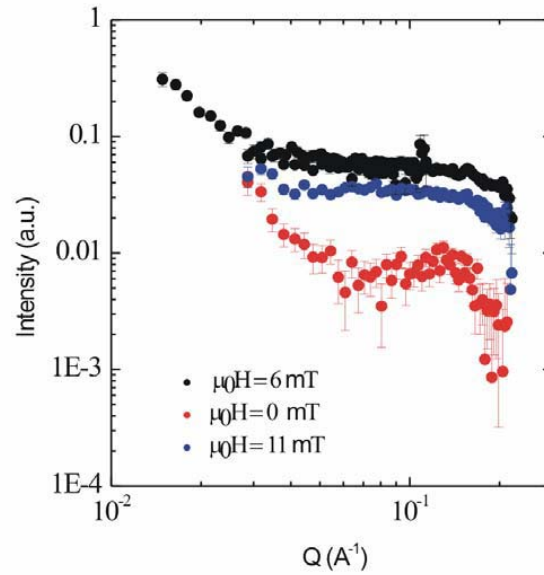


Figure 1. *SANS scattering from a 300 nm thick CCFA film at C8-D2 for 3 different fields.*

References:

- [1] I. Galanakis, P. H. Dederichs, and N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).
- [2] A.D. Rata, H. Braak, D.E. Bürgler, S. Cramm, and C.M. Schneider, cond-mat/0603649.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

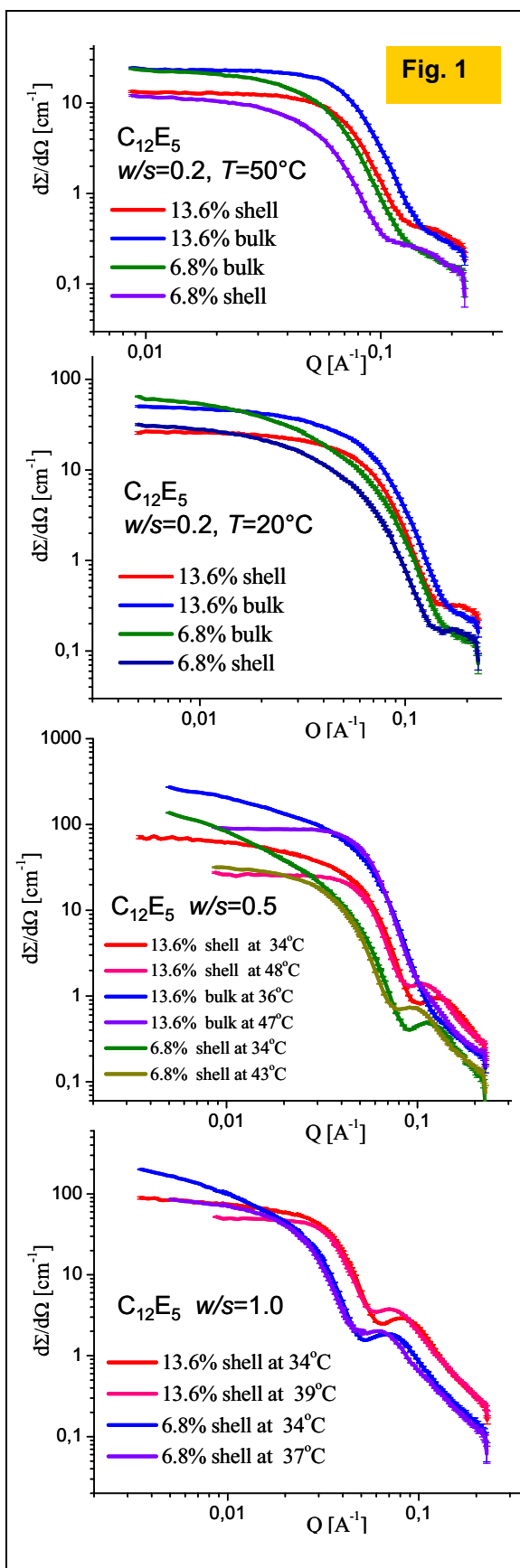
Proposal number:	KW2-05-052		
Experiment title:	Characterization of nonionic w/o microemulsions stabilised by nonionic (and ionic) surfactants as precipitation media for the synthesis of BaCO ₃ nanoparticles.		
Dates of experiment:	16.01. – 17.01.2006 25.02. – 26.02.2006 08.03. – 09.03.2006	Date of report:	19.06.2006
Experimental team: Names	Addresses		
W.F.C. Sager	IFF-Soft Matter, FZ-Jülich P.O. Box 1913, 52425 Jülich IFF-8: Scattering Methods, FZ-Jülich P.O. Box 1913, 52425 Jülich		
M. Feygenson			
Local Contact:	A. Radulescu		

Experimental report text body

In 2003 we started an extended study on understanding crystallization processes of BaCO₃ nanoparticles in water-in-oil (w/o) microemulsions stabilized by nonionic surfactants only or mixtures of nonionic and ionic surfactants. Emphasis was first laid on investigating how far adjusting the compositions and precipitation conditions of the parental microemulsion precursors can be utilized to control the crystal structure, to tune particle morphology and to regulate particles aggregation processes. To be able to gain consistent ideas about the formation of the BaCO₃ nanoparticles in microemulsions of different structure and exchange kinetics, we want to map the BaCO₃ nanocrystals of different morphology onto a more generalized microemulsion structure landscape. For this we have to characterize both the nanoparticles formed by transmission electron microscopy (TEM) as well as the parental microemulsions by small angle scattering (SAS).

Since we found that using the two nonionic surfactants Igepal and C₁₂E₅, a large variety of different nanostructures with well-defined morphologies can be obtained ranging from amorphous filaments, cube and disc shaped meta-stable nanocrystals to witherite type rhombohedral nanocrystals, nanoplatelets, nanoneedles and (ordered) hexagonal nanorods as well as to nanofibres and bundles, it is of special interest to analyse the relationship between microemulsion morphology and particle formation kinetics for the microemulsions employed as precipitation medium.

During our allocated 3 beam times at KWS2 from January to March, 2006, we completed the temperature series started in 2005 for the Igepal and C₁₂E₅ stabilised microemulsions as function of salt concentration (0.1-0.3M salt) and water-to-surfactant ratio ($0.1 \leq w/s \leq 1$). For nonionic surfactants one expects a microemulsion droplet-to-cylinder transition within the one-phase microemulsion region with decreasing temperature and increasing w/s value. To analyse the data recorded we need to adapt the 2-component model for spheres and cylinders, developed earlier for the analysis of scattering curves of AOT stabilized microemulsions [1]. In the case of the nonionic microemulsions, the monomer solubility of the surfactant depends strongly on temperature, which leads to an increase in the droplet radius with increasing temperature. Furthermore we found that the cylinder length depends significantly on the temperature and that especially at $w/s > 0.2$ the low Q part of the



scattering curves is dominated by the structure factor. To obtain the missing information we measured the salt free microemulsions for $C_{12}E_5$ and Igepal at different contrast (bulk and shell) and at lower surfactant concentration and thus lower concentration of the dispersed phase (water and surfactant). These measurements were performed to obtain the necessary information about the thickness of the surfactant layer surrounding the water pools and a better insight into droplet-droplet and droplet-cylinder interactions.

Fig. 1 displays the scattering curves measured for the $C_{12}E_5$ system at w/s values of 0.2, 0.5 and 1.0 with only water as aqueous phase at surfactant concentrations of 6.8% and 13.6%. For the shell contrast measurements a mixture of D_2O and H_2O possessing the same scattering length density as the deuterated oil (continuous phase) was used, while for the bulk contrast measurements the scattering length density of the water phase was matched to the one of $C_{12}E_5$. Since the phase boundaries of the one-phase region depend on the kind and amount of deuterated compound used and the amount of surfactant, *Fig. 1* shows the scattering curves for the highest and lowest possible temperature within the one-phase region for each microemulsion measured. It can clearly be seen that the structure factor becomes important at the $w/s \geq 0.5$ and that significant amounts of longer cylinders are only formed at the higher w/s . At $w/s=0.2$ the dominant contribution to the scattering curves comes from spherical droplets. All w/s values studied show a shift of the scattering curves to smaller Q for the lower surfactant concentration. Since the monomer surfactant concentration depends only on the temperature, less surfactant is available at lower total surfactant concentration that is situated at the interface between the water and oil domains and thus the radii of droplets and/or cylinders become larger. At $w/s=1.0$ the $1/Q$ -dependence of the cylinder form factor is strongly depressed by the structure factor.

Besides the pure nonionic systems, we also started to study microemulsions stabilized by mixtures of one of the two nonionic surfactants and the ionic AOT (sodium di(2-ethyl hexyl)sulfosuccinate). For salt concentrations of 0.3 M we found that upon adding AOT to Igepal stabilized microemulsions by keeping the total amount of surfactant constant the sphere $\leftrightarrow$ cylinder coexistence shifts to the sphere side. While for the pure Igepal microemulsion only long cylinders are observed at low temperature, 50% of AOT is sufficient to transform all cylinders into spherical droplets.

- [1] D.I. Svergun, P.V. Konarev, V.V. Volkov, M.H.J. Koch, W.F.C. Sager, J. Smeets, and E.M. Blokhuis, *J. Chem. Phys.* 113, 1651 (2000).



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-06-002		
Experiment title:	Relating rheology and structural changes using Rheo-SANS		
Dates of experiment:	14.02. - 18.02. 2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink B. Lonetti	IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

We investigated the phase behaviour of star-like micelles formed by the amphiphilic block copolymer poly(ethylenepropylene)-poly(ethyleneoxide), $M_{w,PEP} = 1000$ g/mol, $M_{w,PEO} = 20000$ g/mol, in different water/dimethylformamide mixtures by small angle neutron scattering (SANS) [1, 2] and partly by light scattering and rheology. Changing the solvent composition changes the aggregation number (or functionality), f , of the micelles due to changes in the interfacial tension between the core-forming, hydrophobic PEP and the solvent. This enabled us to construct the experimental equilibrium phase diagram in the packing fraction (η) / functionality (f) representation and compare it to theoretical predictions for regular star polymers. One important feature of the star polymer phase diagram is a re-entrant melting, i.e. a fluid-crystal-fluid transition, which should occur in a limited region of functionalities. This transition is predicted by theory, but until now only little experimental evidence was found.

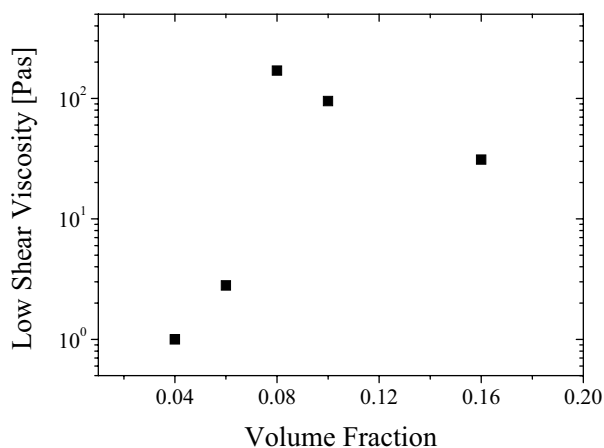


Figure 1: Concentration dependence of the low shear viscosity for star-like micelles.

In our recent rheology experiments on concentrated micellar solutions we observed an anomalous concentration dependence of the viscosity indicating a fluid-solid-fluid transition, see fig. 1. Additional SANS experiments in the same concentration range corroborated this phenomenon with respect to the anomalous concentration dependence of the structure factor peak. We interpret this as an indication for the predicted re-entrant melting and tried to further elaborate these results by supplementary Rheo-SANS experiments to relate in-situ viscosity to microscopic structure.

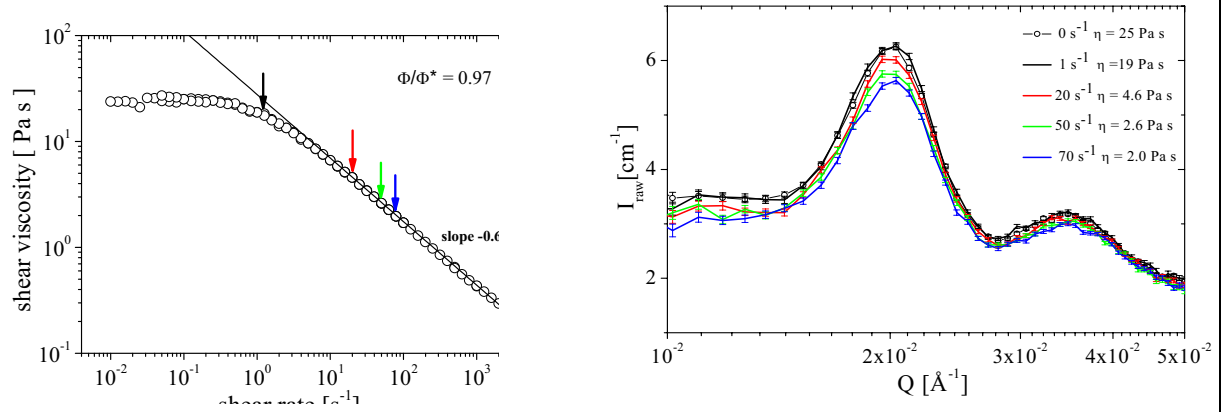


Figure 2: Flow curve (left) and SANS intensity (right) for a micellar solution of volume fraction $\Phi=0.08$ (corresponding to $0.97c^*$).

Figure 2 compares the structure factor $S(Q)$ obtained by Rheo-SANS to the corresponding the flow curve for a micellar solution at a volume fraction $\Phi=0.08$ (corresponding to $0.97 \Phi^*$, with Φ^* the overlap concentration). The flow curve, i.e. the dependence of the shear viscosity η on shear rate $\dot{\gamma}$, shows a strong decrease of η with increasing $\dot{\gamma}$ (approximately 2 orders of magnitude). This gives a limiting power law $\eta \sim \dot{\gamma}^{-0.6}$ in the high shear rate regime. In the microscopic SANS level, on the other hand, only minor changes are observed. In the Rheo-SANS experiments performed in steady shear, the height of the main structure factor peak decreases only slightly with increasing $\dot{\gamma}$. This indicates a loss of local order, but the peak position, i.e. the characteristic particle distance, remains nearly unchanged. Also in oscillatory shear (amplitude sweep) no effects were visible in the SANS data. Therefore a decoupling of the microscopic structure of the sample from its macroscopic flow properties is observed.

References:

1. R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, *Macromolecules*, **37**, 9984, 2004.
2. M. Laurati, J. Stellbrink, R. Lund, L. Willner, D. Richter, and E. Zaccarelli, *Phys. Rev. Letters*, **94**, 195504, 2005.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-003		
Experiment title:	Test of the small detector – 2nd part.		
Dates of experiment:	13.02.2006	Date of report:	09.05.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus	Forschungszentrum Jülich GmbH, IFF, D-52425 Jülich, Germany		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

In this following work to the first proposal KW2-05-039 now a grid is measured in front of the homogenously irradiated detector. This measurement displays the distortions of the detector best, and thus is a hardcore test for the corrections developed for this kind of detector.

As visualized in Figure 1 the irradiated area of the detector appears almost squared although the real area is a circle. The grid points close to the corners appear distorted most when compared to the ideal theoretical grid (indicated in black). The effect of the corrections is displayed in Figure 2. The area of the detector appears bigger and is much closer to a circular shape. All grid points lie much closer on the ideal grid. Nonetheless, some distortions remain, and individual lines of the grid randomly deviate from the theoretical lines. These remaining distortions cannot be treated by a simple mathematical formula. If such distortions shall be corrected in the future one has to triangulate the detector area, and force the originally measured grid on the ideal theoretical grid. The stability of such fine-tuning has to be tested.

All in all, a large step has been done towards the full adoption of the new, small, high resolution detector at the two SANS instruments in Munich.

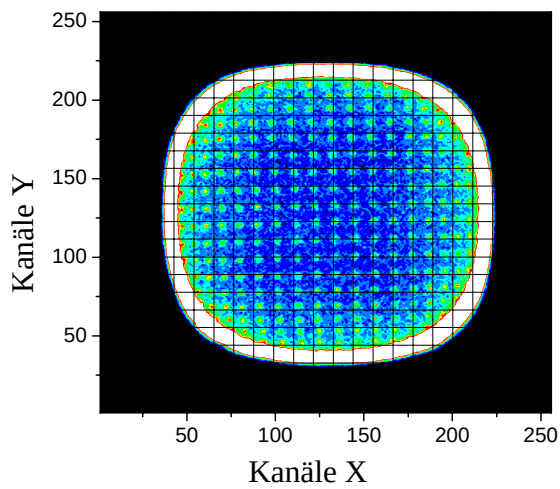


Figure 1: The untreated measurement of a grid in front of the small detector. The grid was homogenously illuminated. One can see the distortions especially at the corners of the irradiated area.

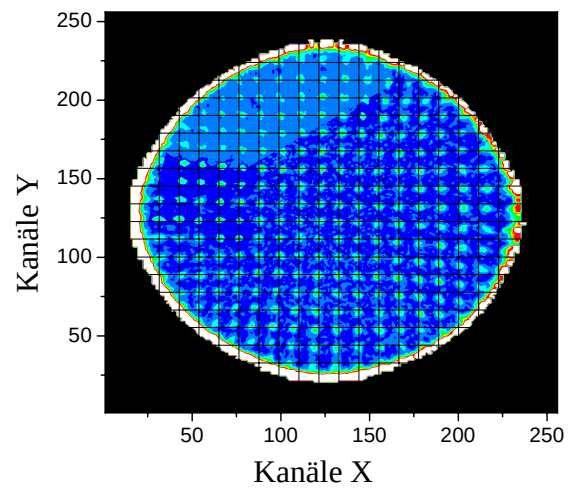


Figure 2: The corrected measurement of a grid. The grid holes are much more regular compared to the theoretical grid in black. Nonetheless some distortions remain, which might be corrected in the future.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-06-004		
Experiment title:	Self-assembling in solution of alternating copolymers of vinyl-tetramethylene (VTM) and methylenecyclopentane (MCP)		
Dates of experiment:	13.02.06 – 16.02.06	Date of report:	29.05.06
Experimental team:			
Names	Addresses		
Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Lewis J.Fetters	School of Chemical Engineering, Cornell University, Ithaca, NY 14853 USA		
Local Contact:	Dr.H.Frielinghaus		

Experimental report text body

Cycloolefin copolymers represent a class of thermoplastic materials of growing interest, with mechanical and physical properties ranging from those of amorphous glasses to those of thermoplastic elastomers. One of the problems of poly(cyclic olefins) is their high melting point T_m and glass transition temperature T_g , which are close to the decomposition temperatures of the polymers. Recent advances in catalyst systems for living olefin polymerization have made possible to synthesize polyolefin-based block copolymers with precisely controlled molecular weight, molecular weight distribution and tacticity. Recently [1], the interest in preparing polyolefin-based materials with an improved thermal properties led to the synthesis of a random copolymer with 1,3-ethylenecyclopentene (MCP) and 3-vyniltetramethylene (VTM) units by polymerization of 1,5-hexadiene. Two such materials generically called RTM4-34 and RTM4-80 were for the first time investigated in solution by SANS in order to obtain information about the radius of gyration R_G of the polymer coils, the molecular weight M_w and the virial coefficient A_2 . For this purpose we investigated different polymer concentrations in dodecane at 30°C by using the KWS2 instrument. Fig.1 presents the scattering cross sections of RTM-34. From the analysis of the scattering cross-sections in terms of the Zimm approximation [2]

$$S(Q)^{-1} = \left[\frac{d\Sigma}{d\Omega}(Q)K \right]^{-1} = \frac{1}{V_w \Phi} + 2A_2 + LQ^2$$

the R_g and the forward scattering $S(0)$ have been evaluated. Further analysis of the inverse forward scattering as a function of the inverse polymer concentration $1/\Phi$ provided the molar volume V_w and the virial coefficient A_2 . Fig.2 presents the Zimm plot of the scattering cross sections and in the inset the evaluation of the V_w and A_2 . The experimental scattering patterns have been well described by the Beaucage form factor [3] using the parameters evaluated by Zimm analysis as is revealed by the fits in Fig.1 (red curves).

The radii of gyration R_G were roughly about 160Å and 155Å while the evaluated molecular weight M_W was about 70K and 33K for RTM4-34 and RTM4-80, respectively.

References: [1] R.T.Mathers and G.W.Coates, Chem.Comm. 422, 2004; [2] A.Radulescu et al., J.Pol.Sci. B 42, 3113, 2004; [3] G.Beaucage, J.Appl.Cryst. 29, 134, 1996.

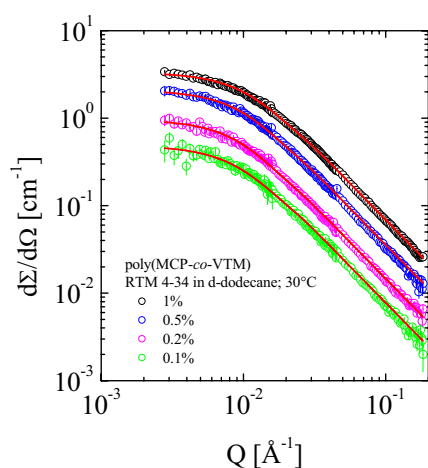


Fig.1 – The scattering cross sections of the RTM4-34 material in dodecane for different polymer concentrations. The red curves represent fits of the experimental data in terms of the Beaucage form-factor.

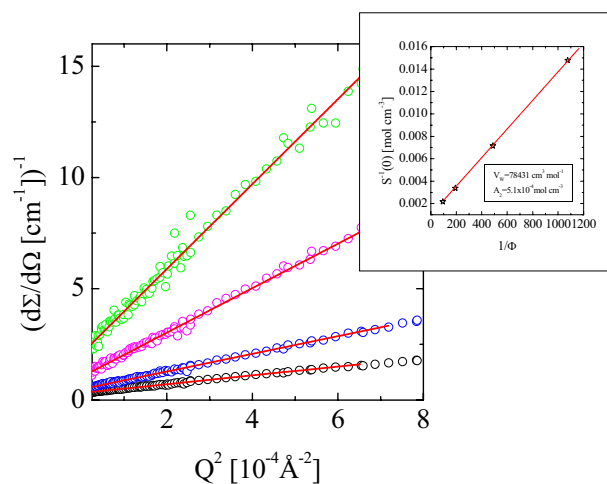


Fig.2 – Zimm plot of the data from Fig.1 and the analysis of the forward scattering providing the molar volume V_w and virial coefficient A_2 .



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-005		
Experiment title:	High resolution polarized GISANS on a polarizing supermirror		
Dates of experiment:	07.02.-12.02.2006	Date of report:	14.06.2006
Experimental team: Names	Addresses		
E. Kentzinger H. Frielinghaus Th. Brückel	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	H. Frielinghaus		

Experimental report text body

As mentioned in report KW2-05-033, polarized GISANS was measured on a remanent polarizing supermirror at C8-D3. The GISANS signal from roughness correlations was well resolved. However, the GISANS signal from magnetic correlations was not well resolved from the Q resolution along the y direction. We present here a tentative to study the magnetic correlations using a longer collimation length and a longer sample-to-detector distance than before, namely C14-D14.

The measurements were performed using the same set-up as the one presented in report KW2-05-032. In Fig.1 we show an example of such a measurement, performed in a field of +5.5 mT after having saturated the sample in a negative magnetic field and at an angle of incidence of the neutrons $\alpha_i = 0.2^\circ$. In both spin channels one observes at $\alpha_i + \alpha_f = 0.4^\circ$ the specular reflection peak. In the spin-up channel, a peak, well resolved from the Q_y resolution, is observed at $\alpha_i + \alpha_f = 0.85^\circ$ (i.e. at $\alpha_f = 0.65^\circ$). It can be correlated with the enhancement of the off-specular scattering measured in the spin flip I+- channel at HADAS at $\alpha_i = 0.2^\circ$ and around $\alpha_f = 0.65^\circ$ (see Fig.2). This peak then originates from the scattering by magnetic correlations. From the width of the peak, much bigger the width of the Q_y resolution function (given by the Q_y width of the specular reflection), we deduce a lateral correlation length of the magnetic correlations equal to 300 nm.

In Fig.2 the range of positive α_f values that can be reached at the chosen sample-to-detector distance is depicted by red vertical lines. As can be seen it does not cover the whole range of α_f values where magnetic off-specular scattering is observed. Moreover, this range gets smaller as the angle of incidence α_i is increased. It therefore does not allow figuring out whether a depth dependency of the magnetic correlation length exists.

This issue is a quite general one at a SANS machine: when one wants to measure with a good resolution in wave vector transfer Q , the detector has to be brought far away from the sample, limiting therefore the range of accessible Q -values. At FRM-II, in order to measure high resolution GISANS at relatively high Q_z values, two ways will be probed:

- 1) Install a high resolution detector (HADAS-type) and reduce the wavelength resolution $\Delta\lambda/\lambda$ (by installing a chopper) on KWS-1.
- 2) Perform GISANS on KWS-3, using a good resolution along Q_y and a relaxed resolution along Q_z (entrance aperture small along the horizontal direction, large along the vertical one).

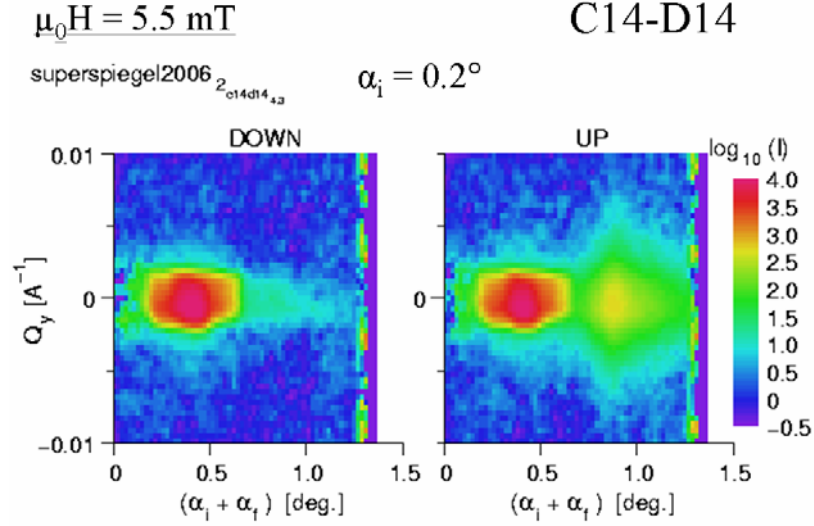


Fig.1: Polarized GISANS signal measured at C14-D14 on a remanent polarizing supermirror. Counting time: 23 minutes per spin channel.

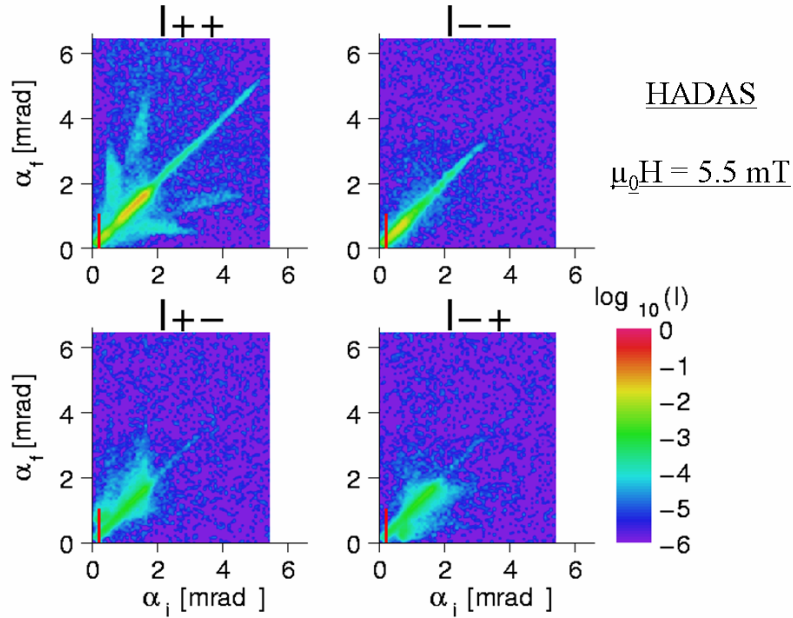


Fig.2: Off-specular scattering of polarized neutrons with polarization analysis measured at HADAS on the same supermirror as above and at the same applied magnetic field $\mu_0 H$.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-008, KW2-06-014		
Experiment title:	Bicontinuous microemulsions in presence of a sticker polymer with an ionic end group – part I, II		
Dates of experiment:	20.03.2006 – 22.03.2006 7.4.2006	Date of report:	11.05.2006
Experimental team: Names	Addresses		
Martin Brodeck Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

Monofunctional sticker polymers have successfully been investigated in earlier measurements (KWS2-05-019). A strong efficiency boosting was found. These sticker polymers consisted of an oil-soluble sticker (several carbon atoms) and a water-soluble polymeric chain. The question is whether a sticker polymer with a water-soluble sticker and an oil-soluble polymeric chain shows the same behaviour regarding the influence on the bending rigidity κ . Two different polymers with an ionic sticker have been investigated. The first of the two, COOH(t-butylacrylate), has an ionic sticker with approximately 50 water-soluble monomers. The second one, monocarboxy terminated polybutadiene, is made up of about 185 monomers. Carboxylic acid forms the sticker of the polymer. Therefore to anchor the sticker to the water-phase NaOH has to be added to the system. The carboxylic acid will dissociate in an alkaline environment. Three different allocations of NaOH and four different polymer concentrations ($\delta=0\%$, 3%, 6%, 10%) have been investigated for the first polymer. For the second polymer with the longer chain only one concentration of NaOH has been studied. Changing the concentration of NaOH will influence the amount of polymers that are able to attach to the interface.

To prepare the neutron scattering experiments phase diagram studies have been conducted on both polymers. In these measurements the phase behaviour is determined depending on the amount of surfactant and the temperature of the system. The minimum amount of surfactant needed to emulsify the system, γ_{fp} , can then be extracted from the temperature vs. surfactant plot. This point, the so-called fish tail point, describes the efficiency of the polymer. Increasing the amount of polymer will decrease the minimum amount of surfactant needed to dissolve all available oil and water. The first of the two investigated polymers shows a relatively small boosting effect, which is probably due to the too short polymer chain. Therefore the second polymer with a longer water-soluble chain has been investigated. This polymer showed a stronger boosting effect, comparable to the efficiency of the polymer with oil-soluble sticker investigated earlier ($C_{12}E_{100}$).

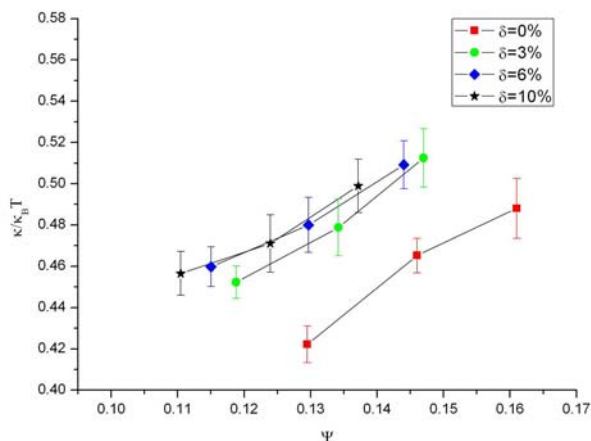


Figure 1: At pH 11.2 there are just enough Na^+ -ions to anchor a polymer amount of $\delta=3\%$ to the interface. Adding more polymer has almost no effect on the bending rigidity κ .

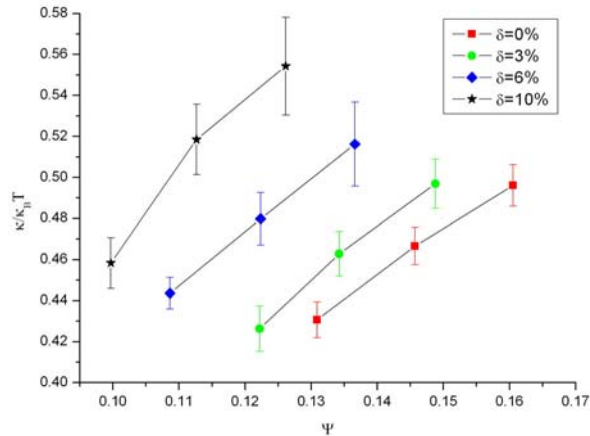


Figure 2: After an increase of the NaOH particles in the system the bending rigidity responds to an increased polymer amount of up to $\delta=10\%$.

The second information extracted from the phase diagram is the change of the spontaneous curvature c_0 . Due to the unsymmetric polymer the change of the spontaneous curvature is balanced by a change of the temperature of the fish tail point. Both polymers behaved as expected with a decreased temperature.

The macroscopically determined phase diagram is connected to microscopically defined parameters of the Helfrich model. The model assumes the elastic properties of the surfactant film to be dominant in the free energy of the microemulsion. The three important parameters are the spontaneous curvature c_0 , and two elastic moduli, namely the bending rigidity κ and the saddle splay modulus $\bar{\kappa}$. The spontaneous curvature decreases with increasing temperature and increases with increasing sticker polymer amount. At the fish tail point the spontaneous curvature is zero, so the two contributions are balanced. The elastic moduli are spatially renormalized parameters with a logarithmic dependence on the surfactant amount. The absolute values of the elastic moduli increase with increasing polymer amount. At the fish tail point the saddle splay modulus is a negligible constant, and so the renormalization is balanced with the polymer term. This balance leads to an exponential dependence of the minimal surfactant amount with respect to the scaled polymer amount.

To obtain the bending rigidity κ with small angle neutron scattering the bulk contrast has been chosen. With the Teubner-Strey-formula the domain size d and correlation length ξ can be extracted from the scattering patterns. The Gaussian random field theory is used to obtain the bending rigidity from these structural parameters. Figures 1 and 2 show the dependence of the bending rigidity on the surfactant amount ψ . Three surfactant amounts in the one phase region have been measured for every polymer concentration. This makes it possible to extract the bending rigidity for one surfactant concentration by extrapolating the data.

For the lowest concentration of NaOH (pH 11.2) only $\delta=3\%$ of the polymer had the possibility to anchor to the interface. Further increasing the amount of polymer to $\delta=6\%$ and $\delta=10\%$ does not influence the bending rigidity κ any more. The polymer floats in the oil phases and the sample looks dim. Figure 1 shows the results of these measurements. Increasing the amount of NaOH to a pH of 12 will allow more of the polymers to stick to the membrane. In this case the bending rigidity is further increased by adding polymer, as can be seen in Figure 2. Even for $\delta=10\%$ enough Na^+ is available. A further increase of the pH value to 13 (ten times the amount of NaOH) will decrease the sensitivity of κ . A polymer amount of $\delta=10\%$ will increase the bending rigidity half as much as the same amount in a pH 12 solution.

The second polymer with longer chain was investigated at pH13. The phase diagram showed a higher efficiency. The neutron scattering experiments have shown that the sensitivity of the bending rigidity has also been increased by the longer polymer chain.

We have shown that the concept of the sticker polymers can be reversed from hydrophobic stickers to hydrophilic stickers. A comparable sensitivity of the efficiency was obtained. Thus, for application a larger set of polymers is accessible.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-009		
Experiment title:	Influence of concentration and ligands on the behavior of Co-Nanoparticles in microemulsions and solutions		
Dates of experiment:	06.03. – 07.03.2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Feygenson Mikhail Pollmeier Klaus	IFF-8: Scattering Methods, FZ-Jülich P.O. Box 1913, 52425 Jülich		
Sager Wiebke Dr.	IFF-Soft Matter, FZ-Jülich P.O. Box 1913, 52425 Jülich		
Local Contact:	A. Radulescu		

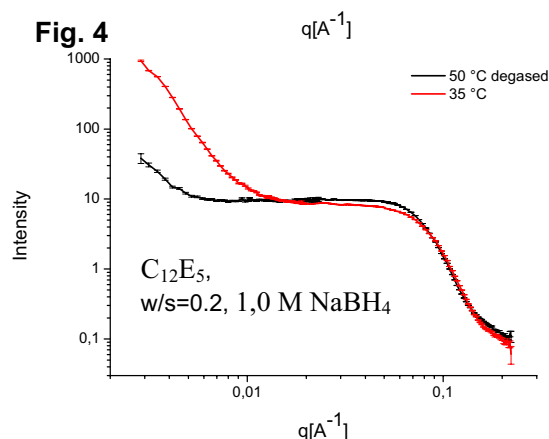
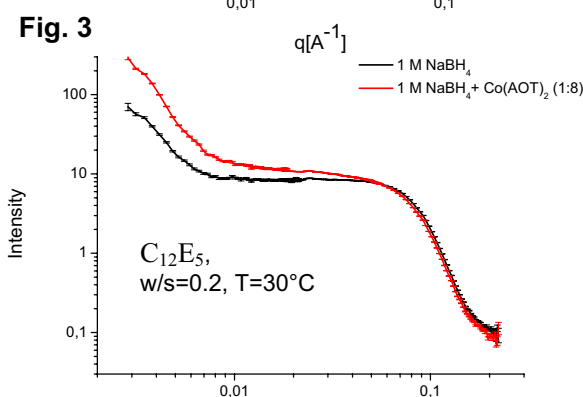
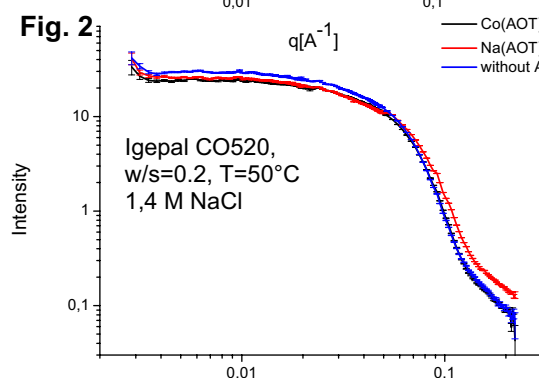
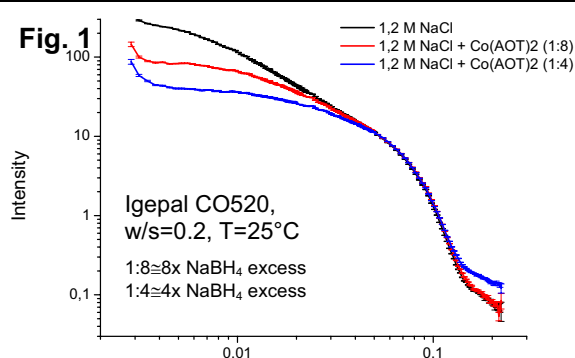
Experimental report text body

Since our final goal aims at measuring magnetic and nuclear form factors of magnetic nanoparticles in solution and to thus determine the average magnetization density within single particles, we have been working from May 2005 onward on developing microemulsion- or micelle-based synthesis routes for magnetic cobalt nanoparticles with well-defined size distribution and tunable size as well as particle interaction.

In literature, there are basically two major routes described to synthesize magnetic Co-nanoparticles. The first route is based on the thermal decomposition of cobalt carbonyl compounds in a suitable surfactant/ligand environment (see, e.g. [1]), and requires high temperatures and/or high pressures and toxic starting compounds. The second route, originally proposed by Pileni et al. [2,3], employs water-in-oil (w/o) microemulsions as nano-structured reduction medium. Pileni and coworkers used as surfactant the double tailed NaAOT (sodium *di(2-ethylhexyl) sulfosuccinate*) in which the sodium ions were either partially or completely exchanged by cobalt ions. Co-nanoparticles were obtained by adding the reducing agent NaBH₄ solubilized in a NaAOT stabilized w/o microemulsion or directly as aqueous solution. Since we encountered, using the Pileni routes, low yields [2] or phase separation problems [3] that led to undefined reduction and particle formation, we started in 2005 to investigate the incorporation of nonionic microemulsions in the synthesis route. This allowed us to study the formation of Co-nanoparticles over a wider concentration and temperature range and to thus access a larger parameter space for particle morphological fine-tuning.

The Co-nanoparticles were prepared by employing w/o microemulsions that were stabilized by nonionic surfactants of the ethoxylated alkyl- or arylether series such as C₁₂E₅ and Igepal CO520 and contained NaBH₄ of different concentration in the aqueous cores. To these microemulsions different amounts of a reversed micellar solution of Co(AOT)₂ in a toluene/hexane solvent mixture can than easily be added in a controlled manner without leading to phase separation and undefined preparation conditions.

In order to (i) understand the Co-nanoparticle formation process within the w/o microemulsions used, to (ii) analyze the main factors that determine particle size and polydispersity and to (iii) study the role of the micro-



emulsion during particle formation, we need to characterize the morphology of the microemulsions as function of salt content, water-to-surfactant ratio (w/s) and temperature before and after addition of Co(AOT)_2 and to record changes occurring during the Co-particle formation process.

For the nonionic w/o microemulsions we expect within the one-phase region spherical microemulsion droplets just below the upper phase boundary (solubilization limit), above which the w/o microemulsion expels (excess) water. With decreasing temperature the droplets transform gradually into cylinders, whereby volume fraction and cylinder length depend strongly on the surfactant used. Generally the C_{12}E_5 stabilized microemulsions appear to be more stable against the droplet-to-cylinder transition than the Igepal stabilized ones. In order to study changes of the microemulsion morphology occurring upon the addition of different amounts of Co(AOT)_2 , we first had to find out how we can mimic the NaBH_4 solutions with NaCl in order to prevent particle formation and thus be able to study the Co(AOT)_2 influence independently from the changes occurring during nanoparticle formation.

In August 2005 we, therefore, started our SANS-investigation at KWS2 on characterizing the morphology of the microemulsions involved in the Co-nanoparticle synthesis by finding the NaCl concentration which displays the same dependence of the scattering curves with temperature and thus the same microstructural response as a 1.0M NaBH_4 containing microemulsion. We found that for Igepal as well as C_{12}E_5 stabilized microemulsions at two different w/s values of 0.2 and 0.5 a 1.2M NaCl solution can quite well be employed for mimicking.

In March 2006 we looked at the influence of AOT addition on the structure of the nonionic microemulsion and on reactions leading to Co-nanoparticle formation. Fig.1 displays the scattering curves for an Igepal stabilized microemulsion at $w/s=0.2$ and $T=20^\circ\text{C}$. It clearly shows that the addition of Co(AOT)_2 shifts the sphere-cylinder equilibrium to the sphere side which would correspond to an increase in temperature. At high temperature the changes upon AOT addition are less pronounced and there is only little difference between adding Co(AOT)_2 or NaAOT at constant AOT concentration (see Fig.2). Fig.3 shows a reaction induced in a C_{12}E_5 stabilized microemulsion containing 1M NaBH_4 at $w/s=0.2$ and $T=30^\circ\text{C}$ by adding Co(AOT)_2 in a molar ratio of $\text{Co}^{2+}:\text{BH}_4^-$ of 1:8. Differences before and after performing the reaction show up only at very low q and can be associated to H_2 bubble formation which also occurs when NaBH_4 reacts with water only. In this case bubble formation is significantly reduced after degassing (see Fig 4).

- [1] V.F. Puentes, K.M. Krishnan, A.P. Alivisatos, *Science* **2001**, 291, 2115
- [2] C. Petit, A. Taleb, M.P. Pileni, *J. Phys. Chem. B* **1999**, 103, 1805
- [3] I. Lisiecki and M.P. Pileni, *Langmuir* **2003**, 19, 9486



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

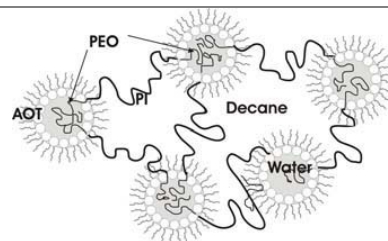
Proposal number:	KW2-06-010		
Experiment title:	Conformation of Network-Forming Triblock-Copolymers in Water-In-Oil Microemulsions		
Dates of experiment:	22.04 – 23.04.2006 (reactor shutdown 22.04)	Date of report:	02.06.2006
Experimental team: Names	Addresses		
Tinka Spehr	Technische Universität Darmstadt Institut fuer Festkörperforschung Hochschulstrasse 8, 64293 Darmstadt	Institut Laue-Langevin 6, rue J.Horowitz F-38024 Grenoble F-38024 Grenoble	
Thomas Blochowicz	Technische Universität Darmstadt Institut fuer Festkörperforschung Hochschulstrasse 8, 64293 Darmstadt		
Local Contact:	Henrich Frielinghaus		

Experimental report :

The ternary microemulsion composed of the anionic surfactant AOT, water and decane as oil forms a droplet phase that is stable over a wide range of compositions in the vicinity of room temperature [Kot]. As the radius depends on a first approximation linearly on the ratio of water to surfactant [Dij], size and density of the droplets are independently tunable.

The addition of the amphiphilic triblock-copolymer PEO–(polyethyleneoxide, hydrophilic) –PI (Polyisoprene, hydrophobic) – PEO is assumed to lead to a transiently linked network (see sketch to the right).

The following experiments were planned:



- (1) measurement of the scattering of **pure microemulsion** with shell contrast to determine the droplet form factor
- (2) measurement of the scattering of **PI-homopolymers in d-decane** for comparison with the scattering of network forming polymers
- (3) matching of the scattering length densities of water/heavy water, decane/d-decane to those of PEO and AOT to measure the scattering of the PI-middleblocks (**triblock-copolymer in microemulsion**)

Due to a shutdown of the reactor the main objectives of the experiment could not be achieved. Only some of the prepared samples have been measured. Because of the reduced time only empty beam was measured for background subtraction.

RESULTS:

1. pure microemulsion

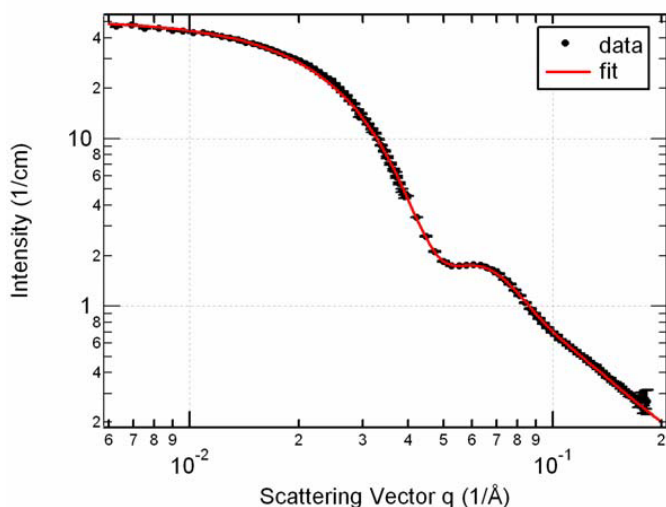


Fig. 1: Scattering from microemulsion droplets in shell contrast, fit of core-shell form factor taking into account polydispersity in size and structure factor for hard sphere potential

parameter	fitted value
radius _(watercore)	56.4 Å
shell thickness _(AOT)	5.9 Å
total radius	62.3 Å
polydispersity	24.1 %

The pure microemulsion (water to surfactant ratio $\omega = 40$, droplet volume fraction $\Phi = 0.14$) under shell contrast was measured at 288 K.

Data has been acquired under the following instrumental settings: C8D8, 30 min and C4D2, 10 min.

The obtained structural information (see table) completes earlier results obtained by small angle X-ray scattering measurements.

2. PI homopolymer in d-decane

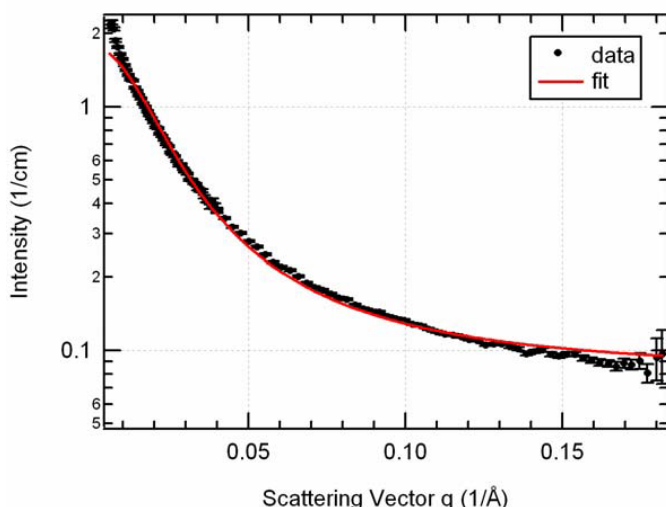


Fig.2: Scattering from PI homopolymers dissolved in deuterated decane, Debye fit

parameter	fitted value
radius of gyration	86 Å

The Polyisoprene (PI) homopolymer (43400 g/mol) was dissolved in d-decane.

Data has been acquired under the following instrumental settings: C8D8, 190 min and C4D2, 15 min.

Due to missing background measurements only preliminary data analysis is possible. The disagreement of data and fit for small q-vectors might indicate that parts of the PI are cross-linked.

3. PEO-PI-PEO triblock-copolymer in microemulsion

No results have been obtained. Weak contrast between the PI-chains and the matched microemulsion requires longer measurements and accurate background subtraction. The matching of water cores and decane matrix to the AOT shell was possible. This information will help for future experiments on this system

[Dij] M. v. Dijk, M. v. Struis, J. Joosten, Y. Levine (1989), *J. Phys. Chem.* **93**, 2506

[Kot] M. Kotlarchyk, S. Chen, J. Rouch, P. Tartaglia (1984), *Phys. Rev. Lett.* **53**, 941



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-011		
Experiment title:	Study of self-assembling peptides		
Dates of experiment:	20.04.2006	Date of report:	06.06.2006
Experimental team: Names	Addresses,		
Dr. Paduano Luigi,	Chemistry Department University of Naples "Federico II" Naples, Italy		
Local Contact:	Dr. Aurel Radulescu		

Experimental report text body

Bio-molecule self assembling is a functional (sometimes pathological) property. Proteins, peptides and all bio molecules interact and self-organize to form well-defined structures able to display specific functions. In the recent years the study of the basic principles underlying the biological processes of self-assembly has largely increased. The sequence named EAK16,1 (Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys)², has shown a strong propensity to adopt a beta-sheet structure and to spontaneously form, in presence of salts, membranes completely non toxic and resistant to proteolytic digestion. A proposed model for membrane produced by molecules such as EAK16 stays on layers of parallel (or antiparallel) β -sheets held together on one side by hydrophobic bonding and on the other side by ionic bond between charged residues. Here we focus on a series of EAK-16 analogues (16- (Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys)² and 8-mer (Ala-Glu-Ala-Glu-Ala-Lys-Ala-Lys) peptides) designed to decode the role of charge and hydrophobic factors in modulating the self-assembling properties.² NMR and CD analyses of a suite of a 16-mer and 8-mer self-assembling peptides were undertaken in order to correlate conformational properties and self-assembling propensity of the monomers. NMR measurements reveal, in particular, that some of the 16-mer peptides form aggregates insoluble or too large to contribute to the NMR spectra (high nuclear relaxation rates) while the 8-mer peptides appear to be free in solution even though able to adopt, in some amount, β /extended structures. For the 8-mer peptides with the highest hydrophobic character in the series, the β - structure is definitively evidenced by the relative intensities of NOE contacts.

In this context, SANS test measurements have allowed obtaining some information on the aggregates formed by the two samples (16- and 8-mer peptides). As shown in Figure 1a at the concentration explored there is a low presence of aggregates. The scattering intensity is quite flat except for a slight probably increase at low q .

At the same concentration (see Figure 1b) the 16-mer sample shows a cooperative tendency of the molecule to self assemble. $I(q)$ shows a q^{-1} decay typically of cylindrical structure whose length is above 900 Å. This suggests that 16-mer peptides probably stick one on top of the other forming supramolecular aggregates whose shape is geometrically similar to rod.

Further measurements at different concentration and environmental condition should allow gaining detailed information of their structure.

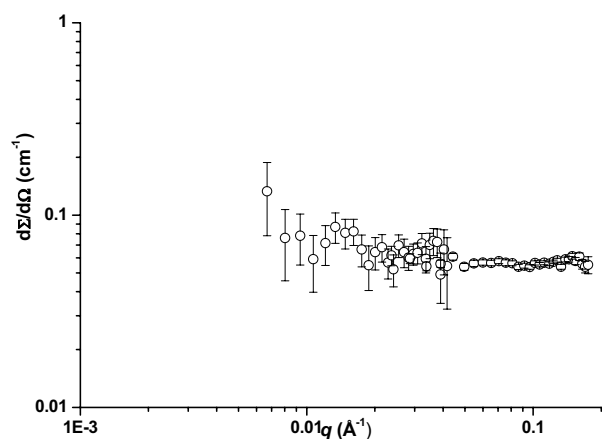


Figure 1a – Scattering cross sections measured at 25°C for the sample 8-mer

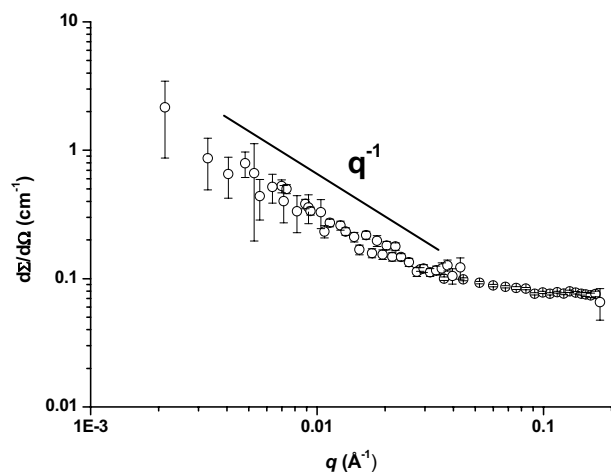


Figure 1b – Scattering cross sections measured at 25°C for the sample 16-mer



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-06-012		
Experiment title:	Benchmarking test on KWS-2 prior to move to Munich		
Dates of experiment:	01-02.05.06	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus Wim Pyckhout-Hintzen Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.H.Frielinghaus		

Experimental report text body

Several test investigations on benchmarking materials and materials of interest for instrumentation development have been performed at KWS-2 instrument prior to its movement to Garching at FRM-2 reactor.

1. The absolute scattering of X-ray machines is not often exploited. Therefore some practical samples are sought which scatter well enough and rather peaked so that the long time sampling of data can be avoided. A fluorinated commercial film is tried which was calibrated in SANS. The contrast is given by amorphous and crystalline regions and a typical polydisperse spherical form factor with small contributions from a hard-sphere interaction can be noticed (Fig.1). The neglect of the structure factor amounts up only to 5% in the peak and the sample can be readily applied in the accessible Q-range of the X-ray machine. From the maximum intensity a relation can be extracted from which SAXS intensities can be derived absolutely. This will depend on the power and current of the generated X-ray beam.
2. Of an extreme importance in designing a neutron scattering instruments are the entrance and end-of-guide windows which, in order to optimize the flux of the instrument, must remove as less as possible neutrons from the transported, transmitted or scattered beams. Two potential materials for neutron windows have been tested from the point of view of efficiency in the transmission of neutrons: Zr foil and Sapphire plate. Several thicknesses of both materials have been investigated at KWS2 instrument with regards to scattering and transmission as a function of the neutron wavelength. One could conclude that both materials reveal for a proper thickness of technical interest a very good transmission (higher than 97%). Sapphire shows a very weak scattering and transmits most of the beam while the Zr foils show a strong small angle scattering (Fig.2) which comes from the scattering on grains, the material

being polycrystalline

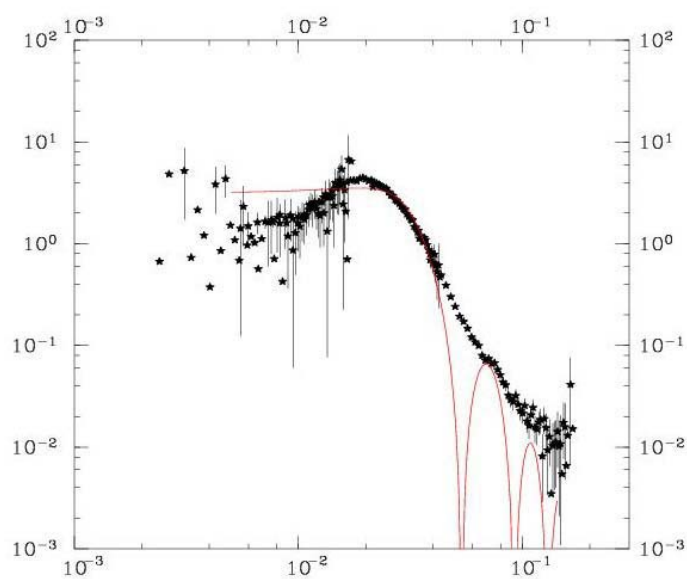


Fig.1 – Scattering cross section of fluorinated commercial film

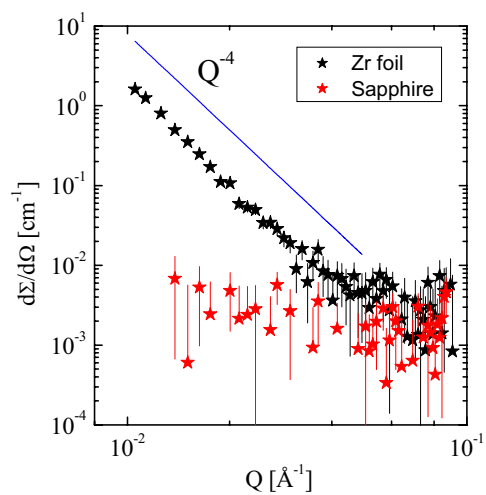


Fig.2 – Scattering cross sections of sapphire and polycrystalline Zr.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-015		
Experiment title:	Bicontinuous microemulsions in presence of polyelectrolytes		
Dates of experiment:	27. – 29.04.2006	Date of report:	11.05.2006
Experimental team: Names	Addresses		
Martin Brodeck Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Henrich Frielinghaus		

Experimental report text body

After measuring polymers with an ionic sticker (KWS2-06-008 and KWS2-06-014) a further step was taken by investigating polyelectrolytes. The analysed polyelectrolyte consists of a regular (non-ionic) hydrophobic chain (PB – polybutylene) and a hydrophilic chain (PAA – polyacrylic acid). Adding NaOH to the system will influence the behaviour of the polyacrylic acid. Different pH values were investigated, ranging from a 30% allocation of acryl acid molecules (in this case there was only one Na^+ particle for about 3 COOH groups) up to a 800% allocation. We expected a flexible to semi-flexible chain for the low allocation and a rod-like behaviour for a roughly 100% allocation due to the repelling charges. Further increasing the NaOH amount should result in a screening-effect of the negative oxygen-atoms at the chain and therefore a flexible to semi-flexible chain behaviour should be retained. Four different polyelectrolyte concentrations have been investigated ($\delta=0\%$, 1%, 2% and 3%) and the choice of the different pH values made it possible to compare different polyelectrolyte concentrations at constant allocation.

Prior to the neutron scattering experiments phase diagram measurements have been performed. They worked well for allocations of about 100% and above, lower concentrations of NaOH and therefore lower occupation resulted in abnormal behaviour of the phase boundaries. A one phase region was found for these allocations even for surfactant concentrations of down to 4%, but the typical fish-like shape was not retrieved. Instead, the upper phase boundary changed rapidly with the amount of surfactant, even increasing with lower concentration. It was particularly interesting to investigate the influence of the polyelectrolytes with these low allocations on the bending rigidity κ .

The bending rigidity κ can directly be measured with small angle neutron scattering. Therefore the bulk contrast is chosen by using deuterated water. The Teubner-Strey-formula can then be fitted to the scattering-curve (Figure 1) and two structural parameters, the domain size d and the correlation length ξ , are obtained from this fit. According to the Gaussian random field theory the bending rigidity κ is connected to these two structural parameters by $\kappa/k_{\text{B}}T = 0.85 \xi/d$.

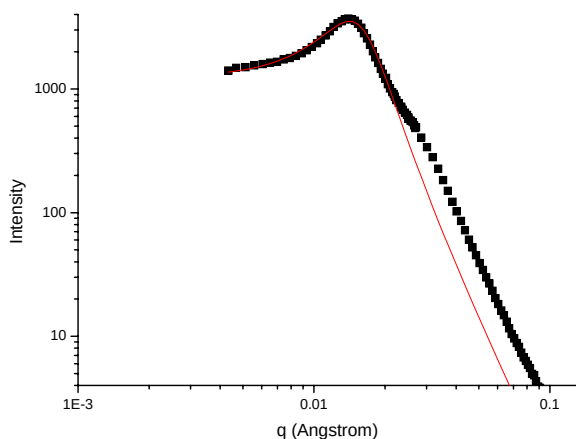


Figure 1: At typical scattering curve. By fitting the Teubner-Strey-formula the two structural parameters d and ξ can be extracted. The bending rigidity κ can then be calculated with the Gaussian random field theory.

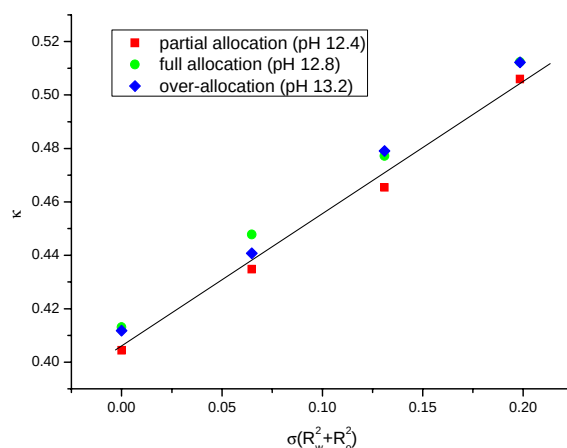


Figure 2: The bending rigidity κ depending on the scaled polymer amount. R_w and R_o are the end-to-end distances of the water-soluble and oil-soluble part of the polymer estimated for ideal chains (no charge effect).

36 samples have been prepared and measured, varying in polymer concentration δ , allocation (influenced by the pH value) and surfactant concentration. For the four different polymer concentrations δ three pH values have been examined: pH 12.4, pH 12.8 and pH 13.2. Changing the polymer concentration at a constant pH value also changes the allocation of the polyelectrolyte.

It was expected to find a lower sensitivity for the full allocation of the chain compared to lower and higher allocations. In this case roughly all COOH groups should have dissociated in the alkaline environment. The repelling charges would then stiffen the polymer and decrease its effect on the interface and the bending rigidity. Against these expectations the bending rigidity does not seem to be majorly influenced by the pH value of the solution. All three NaOH concentrations show similar behaviour (Figure 2). The bending rigidity was extracted for a constant surfactant concentration of 12%. This result is particularly interesting since the phase diagram studies have shown different behaviour depending on the allocation.

A possible explanation could be the limited domain size. The end-to-end distance of these polymers in the mushroom-regime is roughly 60 Å. A stretched polymer, which is significantly larger, would not fit into the domains the size of which ranges from 250 to 500 Å.

The sensitivity of the polyelectrolytes can be extracted from the slope of the SANS measured bending rigidity (Figure 2). We have seen a strong boosting for small polymer amounts. These first impressions have been confirmed by the SANS measurements. The sensitivity of the bending rigidity is about 50% stronger than for regular diblock copolymers.

The SANS experiments have revealed that, against the expectations, the ion allocation of the chains does not influence the bending rigidity. This result considers just the polymer amount to be dominating and neglects changes of the actual size of the polymer as really described by the theory. The consideration of the real size of the polymers is not possible at the present stage, since we simply did not measure the corresponding homopolymer size in a water/NaOH solution. It is furthermore astonishing, that (a) the polymer boosting effect is about 50% stronger for the polyelectrolyte compared to non-ionic polymers (based on a constant size assumption) and that (b) for low charge allocations the phase diagrams seem to open up and resemble to temperature insensitive phase diagrams as obtained for sugar based surfactants or ionic/non-ionic surfactant mixtures. Especially the last example (ionic/non-ionic surfactant mixtures) might have something in common with the polyelectrolyte containing microemulsions. Future work and thinking will shed more light on the current interesting results obtained so far.



Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW2-06-016		
Experiment title:	Investigation of dPS-PB diblock copolymer cylindrical phase with GISANS		
Dates of experiment:	20.04.-21.04.2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
D. Korolkov E. Kentzinger L. Willner	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Denis Korolkov		

Experimental report text body

Nanosized components hold considerable promise as forming the platform for an entirely new type of hardware technology. In such a future technology quantum effects in the nanoobjects might give rise to new functionalities. Sample preparation represents a major challenge.

Two fundamentally different methods are possible: the top-down approach of electron-beam- or interference-lithography or the bottom-up approach of using self-organised soft matter templates.

In our work we used self-organization as the most interesting and fast method for nanostructure fabrication. It allows us to produce nanostructures with a periodicity smaller than 50 nm on a large surface area. Selforganization of a diblock-copolymer with one deuterated component was used: dPS (deuterated polystyrene)-PB (polybutadiene). The ratio of the molecular weights of the two chains was chosen to be 20%/80%. After spin-coating on the Si substrate with native oxide layer and annealing in argon atmosphere samples self-organized into a cylindrical phase. Varying the thickness of the sample with different concentration of solutions and spin-coating speed it is possible to obtain two kind of alignment of the nanostructure: parallel to the surface and perpendicular. In Figure 1 one can see AFM images which don't give any information about bulk. But it is well known that in the case of cylindrical phase there is a thin layer of PS which covers Si wafer.

To explore the possible multilayer structure and the average period between cylinders parallel and perpendicular to the surface, we investigated two samples with different alignment of cylinders, whereby a sample with perpendicular cylinders was obtained from 0.5% solution and had thickness of about 20 nm. All measurements were performed at a wavelength of 6.3 Å.



Figure 1. AFM images of dPS-PB diblock copolymer after annealing. (left) Cylinders are perpendicular to the substrate. (right) Cylinders parallel to the substrate.

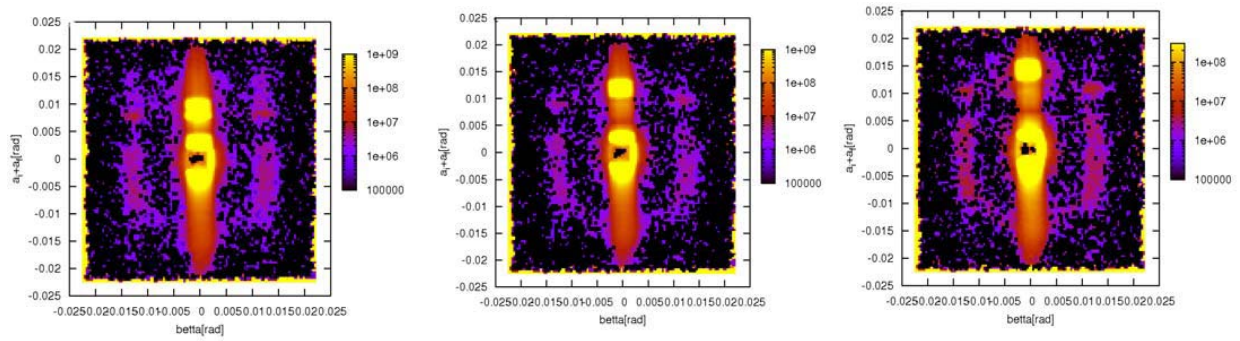


Figure 2. GISANS data of parallel cylinders, measured at different incident angles (from left to right: 0.35, 0.45, 0.55 deg.) for two hours each. Collimation and detector distances are 8m and 11 m respectively.

During our beam time we were only able to perform experiment at collimation distance of 8m and detector distance of 11m. Other distances could not be measured due to a KWS-2 computer problem. The measured GISANS data at different incident angles is presented in Fig.2. It is clear that diffuse peaks on both sides of a specular peak correspond to the lateral structure (parallel cylinders). Diffuse peaks are additionally modulated by reflectivity at low incident angle, because reflectivity terms for both incoming and outgoing wave have maximum near the angle of total reflection. Increasing an incident angle one can see that this modulation becomes less intensive, which is found to be in good agreement with theory. Additionally at an incident angle of 0.55° one can see that Yoneda peak below specular reflection appears. This fact allows to define exactly the intensive part of diffuse peaks as Yoneda peaks too, because they have the same position on Q_z axis.

Unfortunately perpendicular cylinders at the same detector distance didn't give any suitable result due to a very thin layer and have to be investigated additionally. Also we were not able to get any multilayer information due to a very low Q_z range. Nevertheless GISANS is still the best method for obtaining average lateral structure information and we are going to use it further in the future.



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-06-017		
Experiment title:	Characterization of nonionic w/o microemulsions stabilised by nonionic (and ionic) surfactants as precipitation media for the synthesis of BaCO ₃ nanoparticles.		
Dates of experiment:	24.04. – 26.04.2006	Date of report:	19.06.2006
Experimental team: Names	Addresses		
W.F.C. Sager	IFF-Soft Matter, FZ-Jülich P.O. Box 1913, 52425 Jülich IFF-8: Scattering Methods, FZ-Jülich P.O. Box 1913, 52425 Jülich		
M. Feyngenson			
K. Pollmeier			
Local Contact:	A. Radulescu		

Experimental report text body

In order to gain more insight into the "templating" role of microemulsions, we started in 2003 to study in detail by transmission electron microscopy (TEM) the formation of BaCO₃ nanocrystals within the one-phase region of different nonionic water-in-oil (w/o) microemulsions stabilized by nonionic surfactants. Adjusting the compositions and precipitation conditions of the parental precursor microemulsions allowed us for the first time to prepare a variety of different nanostructures with well-defined morphology ranging from (stacked) platelets, (self-assembling) rhombohedral nanocrystals, nano-needles, (ordered) hexagonal nanorods to nano-fibres and -bundles. Since we are interested in analysing the key parameters that determine the crystal size and shape and to investigate the underlying mechanisms of particle nucleation, growth and (orientational) coalescence, it is a prerequisite to determine the microstructure of the microemulsion before and during the reactions performed. This will finally provide a better basis for the theoretical description of crystallization process performed in confined but highly dynamic media.

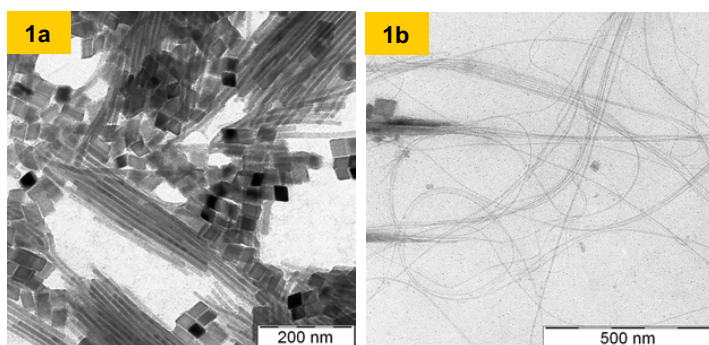


Fig.1: Nanoparticles formed after 5 min at 50 (a) and 23°C (b) in microemulsions stabilised by C₁₂E₅ containing 0.1M salt.

In April 2006 we investigated the microstructure of the parental microemulsions before and after mixing by SANS for microemulsions stabilized by Igepal CO520 or C₁₂E₅ containing 0.1-0.3M salt at high (just below the upper phase boundary of the one-phase microemulsion region) and low temperatures (just above the upper phase boundary of the one-phase microemulsion region).

Fig. 2 displays SANS curves recorded during the reactions for the system C₁₂E₅, w/s=0.1 and 0.1M salts at 50 (2a) and at 23°C (2c) together with the curves of the two parental

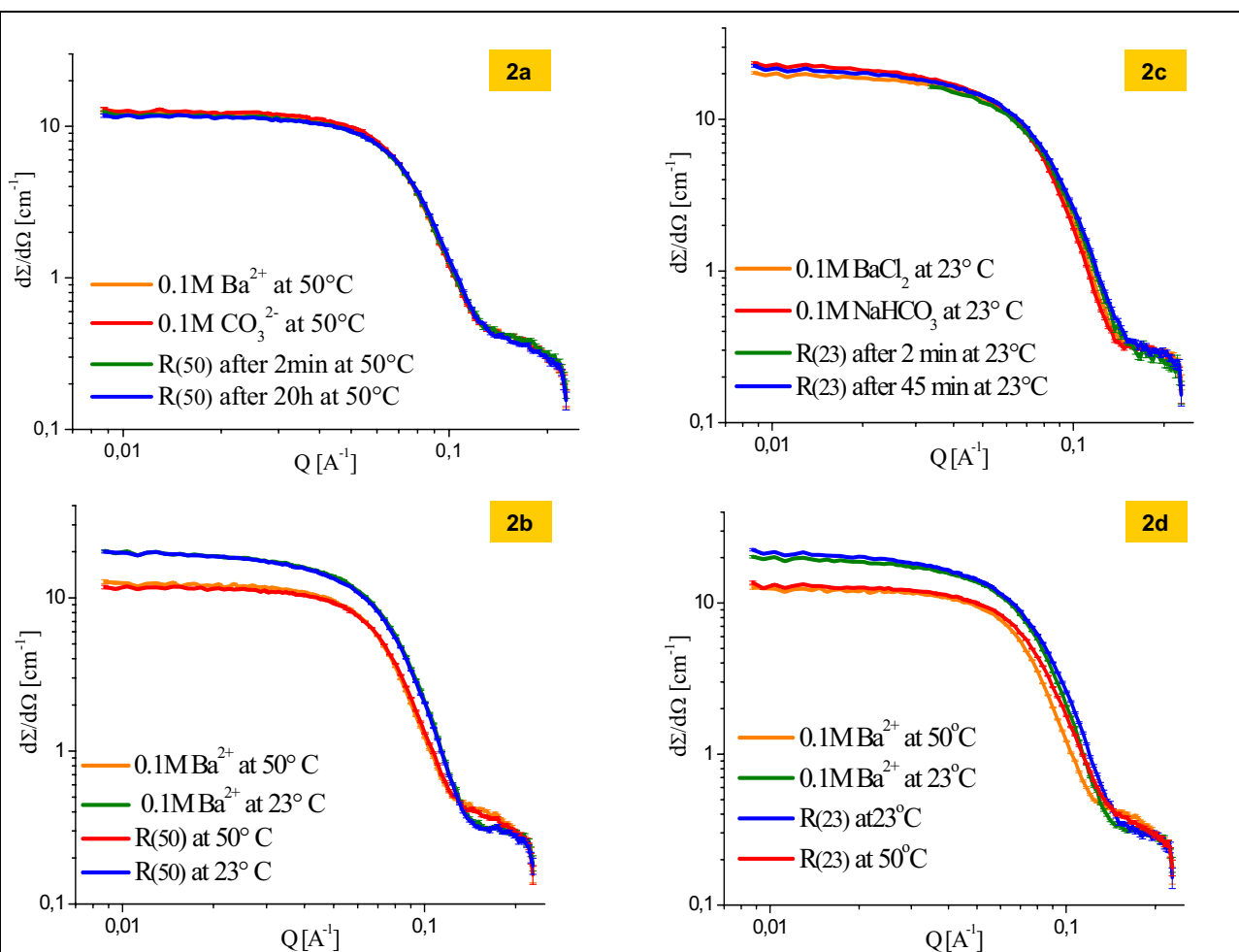


Fig. 2: SANS curves recorded for Ba^{2+} and CO_3^{2-} -containing microemulsions before and after mixing. SANS data of the reacting microemulsions were recorded from 2 seconds up to 1 day. The microemulsions were stabilized by C_{12}E_5 , possessed a water-to-surfactant ratio $w/s=0.2$ and were made with 0.1M salt solutions.

precursor microemulsions. At 50°C as well as 23°C the scattering curves obtained for the parental microemulsions overlap completely, indicating that changes observed during the reaction can only be caused by compositional and/or structural changes of the microemulsion occurring during the BaCO_3 crystallization. At 50°C the scattering curves of the parental microemulsions overlap at low and high wave vector Q with the ones obtained for the reaction after mixing (2min delay) and after 20h (2a). As can be seen from Fig.1a, the nanoparticles formed within the microemulsion (nanocubes and fine nanorods) are immediately of crystalline nature. With time the cubes dissolve and only fairly monodisperse rods are formed. To additionally proof that no changes occurred, we changed the temperature of the BaCO_3 containing microemulsion at later stages. The microemulsion in which the reaction has been performed at 50°C responds to temperature changes in the same way as the parental microemulsion (2b). At 23°C changes in the SANS curves between the parental and the reacting microemulsions show up directly after mixing (with 2min delay), but no further changes occur with time (2c). The shift in the minimum to higher Q indicates that the microemulsions lost water, which might be incorporated in the amorphous structures (1b). At 23°C first amorphous filaments form, that transform only slowly with time into larger needles. If the temperature is changed at later stages to 50°C the difference is even more pronounced (2d).



Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW2-06-018		
Experiment title:	Time-resolved SANS for the crystallization from solution of <i>Syndiotactic</i> -polypropylene		
Dates of experiment:	16.04.06-18.04.06	Date of report:	29.05.06
Experimental team: Names	Addresses		
Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.H.Frielinghaus		

Experimental report text body

Crystallization from solution of syndiotactic polypropylene has been investigated by SANS over a wide temperature range [1]. Several solutions prepared for different molecular weights ($M_w=3K, 8K, 43.4K, 61.4K$ and $85K$) and different polymer volume fractions ($\Phi_{pol}=0.5\%$ and 1%) have been measured. The polymer form multilevel large scale aggregates. The complex morphology of these aggregates was resolved by combined conventional SANS and ultra-SANS investigations. At lower length scale (nanometer order) 2-dimensional objects have been identified from the clear Q^{-2} behavior of the scattered intensity. For the high M_w materials almost all polymers were involved in a rapid crystallization event even once it started, just above $40^\circ C$. Since at low Q no deviation from the Q^{-2} slope was observed (a so-called Guinier regime) we concluded that very large platelets (of sizes much larger than $1000\text{\AA}$) are formed. At larger length scale the platelets form a spherulitic-like morphology. On the other way, the low M_w materials have shown a gradual crystallization from solution in decreasing temperature [2]. Nevertheless, they form similar platelets of almost the same thickness which associate also in spherulites, but these have sizes much smaller than those formed in the case of high M_w materials. The lower the molecular weight, the lower the melting point of the polymer thus, temperatures around ambient represent a smaller undercooling from the melting point and consequently, the driving force for crystallization is smaller. This is the reason only part of polymers crystallize at ambient temperatures. In order to obtain new information about the kinetics of crystallization of lower MW sPP polymers from solution new SANS investigations of a 8K material in decane have been performed at the KWS-2 instrument. The study involved an investigation of the time-resolved crystallization of polymers at different crystallization temperatures. Short time (5 minutes) measurements have been performed at a shorter distance sample-to-detector distance (4m) and the evolution of the scattering pattern was monitorized over several hours for every temperature of interest. The crystallization temperatures investigated were $55, 47, 38$ and $20^\circ C$. Before reaching the temperature of interest the sample was heated up to $95^\circ C$ where the single coil regime was observed

(all polymers were in a single-coil conformation) and then cooled down rapidly up to the crystallization temperature of interest. An example of the time evolution of the scattering patterns collected at a crystallization temperature of 55°C is presented in Fig.1. The time evolution of the scattering intensity at the lowest Q value reached in the experiment is presented in the inset of Fig.1 for all crystallization temperatures investigated. The behaviour of this evolution is rather complex and an analysis in terms of possible models of crystallization kinetics is in progress.

References: [1] A.Radulescu et al. Macromolecules 37, 6962, 2004; [2] experimental report KW1-04-061 FRJ2.

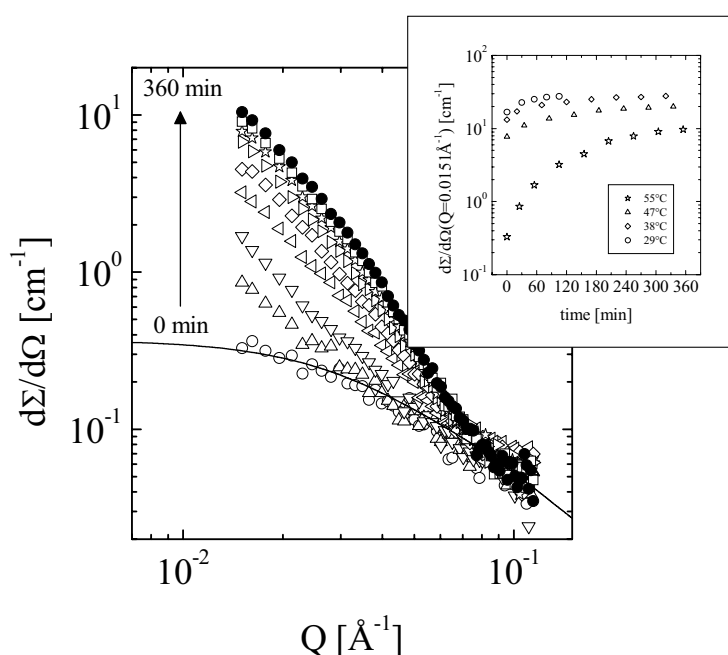


Fig.1 – Time evolution of the scattering pattern from 0.5% sPP 8K crystallizing in decane at 55°C;
the solid curve represents the single coil form factor;
The inset shows the time evolution of the scattering intensity at the lowest Q value
reached in the experiment for the polymer crystallizing at different temperatures