

Small Angle Neutron Scattering Instrument (KWS1)



Instrument Parameters

Beam tube:	NLIIA straight guide; cross section: 4.5 cm (height) $\times$ 3 cm (width)
Monochromator:	velocity selector (DORNIER); $\Delta\lambda/\lambda = 0.2$
Incoming beam - Entrance aperture: - Sample aperture:	variable; suggested: 3 cm $\times$ 3 cm variable; suggested: 1 cm $\times$ 1 cm
Collimation:	length variable from 1 m to 20 m
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 ($\tau_{\text{dead}} = 3 \mu\text{sec}$) 95 % for $\lambda = 7 \text{ \AA}$ 2×10^{-4} (1 MeV)
Neutron flux at sample:	$2 \times 10^5 \dots 2 \times 10^7 \text{ n/cm}^2 \text{ s}$ depending on collimation $\lambda = 7 \text{ \AA}$ wavelength and entrance aperture 3 $\times$ 3 cm ²
Wavelength:	$4.5 \text{ \AA} < \lambda < 15 \text{ \AA}$
Momentum transfer range:	$10^{-3} \text{ \AA}^{-1} < Q < 0.2 \text{ \AA}^{-1}$ optional $Q_{\text{max}} \cong 1 \text{ \AA}^{-1}$
Ancillary equipment:	automatic sample holder in vacuum and air; heating devices: -40 to 200°C; pressure cell: $p = 1 \dots 2000 \text{ bar}$ / $T \approx -30$ to 200°C; strain rigs and temperature control unit for quenched-elongational studies of melts (liquid N ₂)

Instrument Responsible

Dr. Dietmar Schwahn

Dr. Wim Pyckhout-Hintzen

Tel. +49-(0)-2461-61-6661

Tel. +49-(0)-2461-61-4681

Email: d.schwahn@fz-juelich.de

Email: w.pyckhout@fz-juelich.de



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

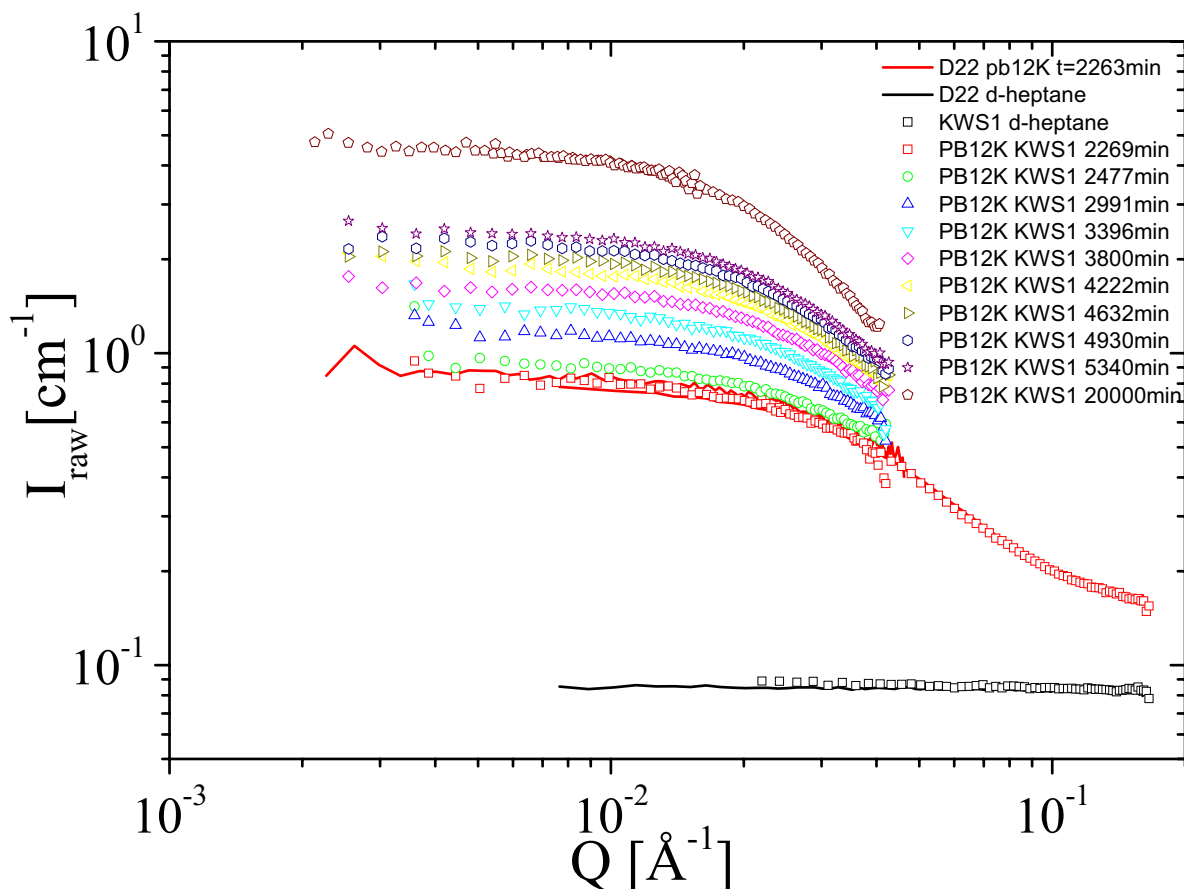
Proposal number:	KW1-04-036, KW1-04-084		
Experiment title:	Final stages of living anionic polymerisation		
Dates of experiment:	17.01.-20. 01. 2005 25.01.2005, 04.02.2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink A. Niu	IFF, FZ Jülich, D-52425 Jülich, Germany IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

Anionic polymerisation is one of the key polymerisation techniques yielding well defined polymers both with respect to molecular weight distribution as well as architecture¹⁾. In recent experiments we were able to relate in detail monomer conversion and initiation processes of “living” anionic polymerisation with structural details combining in-situ high resolution ¹H-NMR and in-situ small angle neutron scattering (SANS). The combination of NMR and SANS opens a new realm of research into polymerisation processes, which appear to reveal completely new aspects of this polymerisation mechanism.

This proposal will be a continuation of an experiment recently started using D22 (ILL). There we followed by insitu SANS the structure formation in the initiation period of “living” anionic polymerisation. However, due to the limited beam time at ILL we were only able to follow the polymerisation for 1 ½ days. After the experiment all samples were quenched to -78°C and stored at this temperature, since we have shown that the polymerisation no longer progresses under these circumstances.

In this experiment we used KWS1 to follow the final stages of the anionic polymerisation after warming up the D22 samples again to 8°C, see fig. 1. Here the raw data, i.e. scattering intensity in absolute units [cm^{-1}],



from the last run at D22, at reaction time $t=2263$ minutes, are compared to the runs performed at KWS1 starting with $t=2269$ minutes. Also shown are data for the pure solvent d-heptane which show first of all the reproducibility and quality of absolute calibration ($\leq 3\%$). The data sets from the polymerizing sample nearly fall on top of each other, which proves the ability to quenching the polymerisation at $T=-8^\circ\text{C}$.

References:

- [1] M. Szwarc, M van Beylen, Ionic Polymerization and Living Polymers, Chapman&Hall: N.Y./London (1993)
- [2] A. Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, A. Radulescu, D. Richter, B. W. König, R. P. May, L. J. Fetters, J. Chem. Phys., **122**, 134906, (2005)



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

Proposal number:	KW1-04-040		
Experiment title:	Small Angle Neutron Scattering of Polystyrene Sulfonate Combs		
Dates of experiment:	13/11/04-15/11/04 & 5/3/05-6/3/05	Date of report:	12/12/05
Experimental team: Names	Addresses		
A. Papagiannopoulos	School of Physics and Astronomy University of Leeds Woodhouse Lane LS2 9JT Leeds UK		
Local Contact:	Aurel Radulescu		

Experimental report text body

We performed a small angle neutron scattering study on dilute solutions of polystyrene sulfonate combs of 5 different architectures (**figure 1**). Both main-chain and side-chains consist of highly charged polystyrene sulfonate with Cs as the counterion. Solutions were prepared in D₂O at a concentration of 0.1 mg/ml and were studied with and without added salt. The experiments were run at 3 different camera lengths (2m, 8m and 20m). The form factors of the PSS combs were successfully measured at the full scattering vector (q) provided by KWS-1 (0.002 to 0.2 Å⁻¹) and the data was put together (**figure 2**) with complementary measurements from static light scattering in order to extend the q -range to even lower values (0.0008 Å⁻¹).

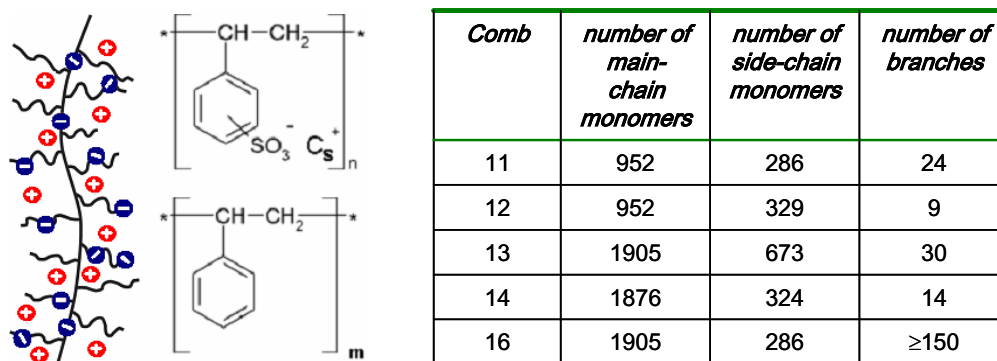


Figure 1: Polystyrene sulfonate comb with the negatively charged monomers and positive counterions. The structure of the monomers is presented which is styrene sulfonate (top) and styrene (bottom) with $n / (n+m) = 85\%$. On the right a table with the characteristics of the different comb architectures is presented.

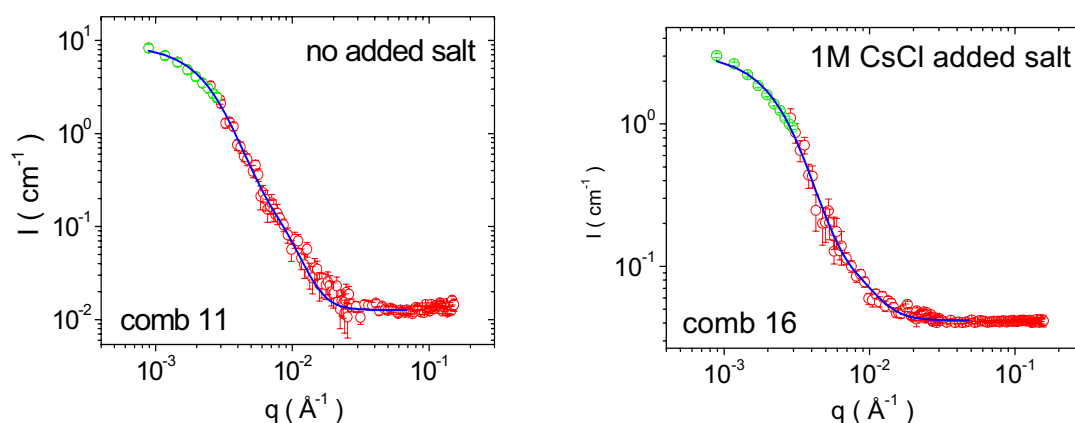


Figure 2: Combined small angle neutron scattering intensity (red) and static light scattering (green) from polystyrene sulfonate combs. The best fits with form factors of cylindrical shapes are shown with continuous lines [1]. Static light scattering profiles have been shifted along the y-axis since the two techniques do not agree in absolute scale.

The cylindrical form factors gave very good fits for all the combs in both cases with or without added salt (**figure 2**). Attempts to fit with other geometries i.e. spheres and ellipsoids did not provide satisfactory fits to the experimentally measured form factors. The dimensions of the cylinders are consistent with linear polyelectrolyte chains that retain their dilute-solution conformation unperturbed, when they are placed on a comb structure. An estimation of the length of the cylindrical comb is $L \approx L_{main} + 2L_{side}$ (**figure 3**), where L_{main} and L_{side} is the length of the main-chain and side-chain respectively, if these chains were free in solution and not attached on a comb. The length of the comb consists of the length of the unperturbed main-chain increased by the length of the unperturbed side-chains, that tilt parallel to the cylinder axis and outwards so that they minimise the repulsive interaction with other side-chains. The radius of the cylinders has been shown to agree with the size of an unperturbed side-chain [1].

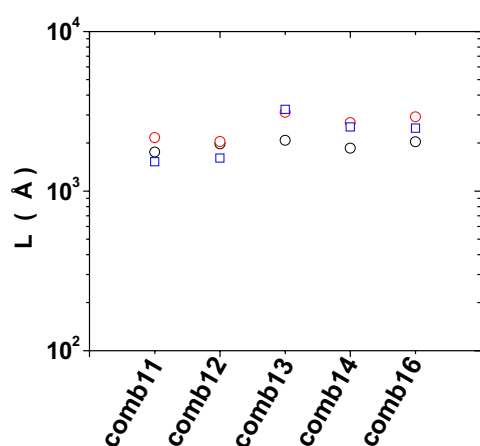


Figure 3: The length of the cylindrical polyelectrolyte combs. The circles are the experimentally observed values for no added (red) and added (black) salt. The error bars are smaller than the size of the data points. The squares are theoretical predictions under the assumption of unperturbed main and side-chains.

The size of a flexible linear polyelectrolyte chain in dilute solution with no added salt can be calculated [2] by the expression, $L_{linear} \approx \frac{nb}{B}$, where n is the number of monomers of the chain, b the monomer length and B the expansion parameter. For polystyrene sulfonate the values $b \approx 3 \text{ Å}$ and $B \approx 3$ where used as they are confirmed to describe the structure of this polyelectrolyte [1,2].

It is also shown (**figure 3**) that the combs decrease in size upon addition of salt, but not significantly, i.e. the size is still comparable with the theoretical prediction for the case of no added salt.

The dimensions of the comb molecules from this study were in agreement with independent measurements of the hydrodynamic radii by dynamic light scattering [1].

References:

- [1] A. Papagiannopoulos, PhD Thesis, University of Leeds 2005.
- [2] A.V. Dobrynin et al., *Macromolecules* **28**, 1859 1995.

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

Proposal number:	KW1-04-062		
Experiment title:	Electrostatic self-assembly of hydrophilic block copolymers		
Dates of experiment:	31.01.05-02.02.05	Date of report:	10.03.06
Experimental team:			
Names:	Addresses:		
Frank Reinhold	MPI für Polymerforschung, Ackermannweg 10, 55128 Mainz		
Local contact:	Wim Pyckhout-Hintzen		

Small angle neutron scattering on complexes of PEO-b-MAA and PAMAM dendrimers

Electrostatic interaction of polyelectrolytes with oppositely charged molecules leads to complex nano-sized structures which can be used as drug delivering systems, templates for crystallisation or for colloid formation of inorganic materials. Therefore many systems have been investigated in that field of research. But polyelectrolyte complexes precipitate if their charges are saturated by the counterions. Therefore it is not possible to build a large variety of structures of these polyelectrolyte complexes in solution. Double hydrophilic block copolymers which are composed of a charged and an uncharged but still hydrophilic block can be used to increase the solubility of polyelectrolyte complexes, because the uncharged block will keep the aggregated structure in solution.

We investigate the complexation behaviour of polyethylene oxide-b-methacrylic acid with NH_2 -terminated PAMAM dendrimers, i.e. large counterions with a size of 1 nm to 15 nm.

Small angle neutron scattering was performed to obtain information about the radii of gyration and the shape of complexes formed by polyethylene oxide-b-methacrylic acid and polyamidoamine dendrimers of generation 4. Samples with an concentration of 2 g/L and different charge ratios λ in deuterated buffer solutions at $pH = 6$ and $pH = 7$. It was measured at detector distances at 20m, 8m, 2m and 1.25m. The calibration was performed with B_4C and plexiglass.

Figure 1 shows the scattering curves at different charge ratios in pH7 buffer solution. One can clearly observe the differences in scattering of aggregated and not aggregated particles. The radii of gyration, calculated by extrapolation of the linear Guinier plots, show a continuous increase in both buffer solutions starting at the radius of the copolymer. Pair distance distribution functions obtained from this measurement by indirect Fourier transformation (figure 2) can reveal information about density and shape of the particles. The comparison with different models shows that the tailing cannot be described by a sphere model, even a polydisperse one. An ellipsoidal shape seems to be the best explanation. The intersection of the function with the x-axis gives the maximum particle dimension (geometrical diameter). It shows the same trend as the hydrodynamic radius from dynamic light scattering data and by calculating the ratio R_G/R one receives again information about the shape of the particles. For a homogenous sphere $R_G = 0.775R$ that means the value 0.65 obtained from the experiment indicates approximately a spherelike structure. This is slightly different to the results of the indirect Fourier transformation, which gives the more detailed information.

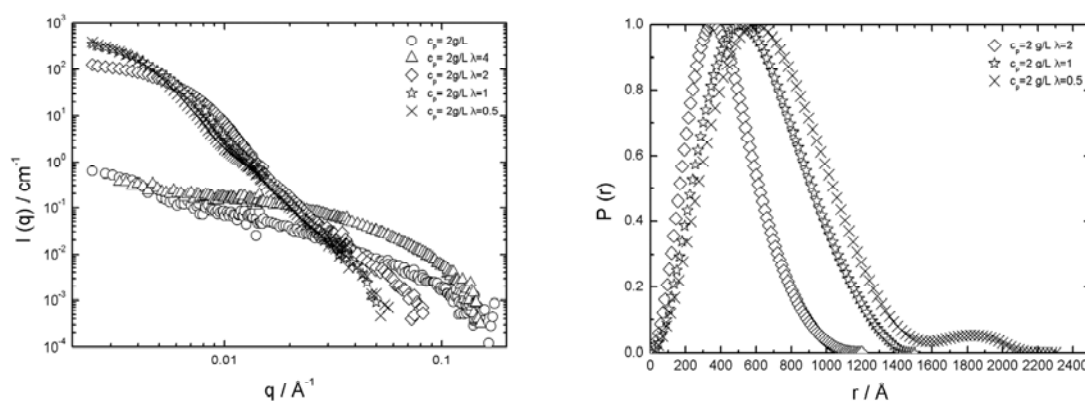


Fig.1 (left side): Scattering curves of PEO-b-MAA and PAMAM-dendrimer G4 in pH7 buffer solution.

Fig.2 (right side): Pair distance distribution functions of complexes formed by PEO-b-MAA and PAMAM-dendrimers in pH7 buffer solution.



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

Proposal number:	KW1-04-065		
Experiment title:	Conformation of the cytoplasmic part of the trasducer		
Dates of experiment:	26.08.2005	Date of report:	28.03.2006
Experimental team: Names	Addresses		
Ivan Budyak	Forschungszentrum Jülich, IBI-2		
Vitaliy Pipich	Forschungszentrum Jülich, IFF		
Georg Büldt	Forschungszentrum Jülich, IBI-2		
Judith Klein-Seetharaman	Forschungszentrum Jülich, IBI-2; University of Pittsburgh, USA		
Local Contact:	Dr. D. Schwahn, Dr. V. Pipich		

Experimental report text body

The SANS measurements were done at the KWS-I instrument at the FRJ-2 research reactor (Research Center Jülich, Germany). A neutron wavelength of $\lambda=7 \text{ \AA}$ with sample-to-detector distances of 2 and 4 m were used to get a range in scattering vector $Q=2\pi/\lambda$ values of 0.01 to $0.2 \text{ \AA}^{-1}$. Protein samples containing 2 and 7.5 mg/ml pHtrII-cyt in dPBS and 5 mg/ml pHtrII-cyt in dPBS + 4M KCl were analyzed at room temperature in quartz cells with 1-mm path lengths. The data were corrected for the detector efficiency, the scattering from the empty cell and solvent, and then radially averaged and calibrated in absolute units by a plexiglas secondary standard. Scattering curves were fitted using the approximation proposed by Beaucage (Beaucage, *J.Appl. Cryst.*, 1996) which combines both the Guinier regime (Guinier and Fournet, *Small Angle Scattering of X-rays*. 1955) and the fractal regime:

$$I(Q) = G \exp(-R_g^2 Q^2/3) + P [\text{erf}(R_g Q/\sqrt{6})]^3 / Q \quad (1)$$

where R_g is the radius of gyration, G is the Guinier prefactor

$$G = \Phi(1-\Phi)V\Delta\rho^2 \quad (2)$$

and P is the amplitude of the fractal part

$$P = \Phi(1-\Phi)\pi^2 r^2 V \Delta\rho^2. \quad (3)$$

Using this equation, the following features can be derived from the curve: (i) the zero Q intercept gives the particle volume if the concentration is known, (ii) the slope of the Guinier region is equal to $-R_g^2/3$ and therefore gives the particle size, (iii) the slope of the mass fractal dimension indicates the shape, (iv) and the Porod region gives the surface area and surface fractal dimension (Beaucage, *J.Appl. Cryst.*, 1996).

We used SANS to complement our observations from analytical gel-filtration and crosslinking experiments, that the cytoplasmic part of the transducer II from *Natronobacterium pharaonis* (pHtrII-cyt) is predominantly monomeric in PBS (Dulbecco and Vogt, *J.Exp.Med.*, 1954) and dimeric in PBS + 4 M KCl. All measurements were carried out in buffers prepared in D_2O to improve the signal:noise ratio.

The concentration-normalized experimental data are plotted in Fig.1 for pHtrII-cyt in dPBS as open circles (○) and in dPBS + 4M KCl as open squares (□). In both cases, the scattering intensity $I(Q)$ follows the scaling law Q^{-1} over a wide Q range of 0.03 to 0.2 $\text{\AA}^{-1}$ (Fig. 1, dashed line). The observation of a $I(Q) \sim Q^{-1}$ dependence is consistent with an elongated (rod-like) shape of pHtrII, both in dPBS and in dPBS + 4M KCl and can be approximated with a cylinder.

The volume fraction of protein Φ was calculated from the ratio between the pHtrII-cyt concentration and the protein density in H_2O , $\Phi = c/d_p$; the volume of the cylinder was assumed to be equal to the molecular volume of protein $V = M/N_a/d_p$. From Eq. 2 and 3, the length and the radius of the protein molecules can be calculated according to:

$$L = \pi G/P \quad (4)$$

$$r = \sqrt{(V/\pi/L)} \quad (5)$$

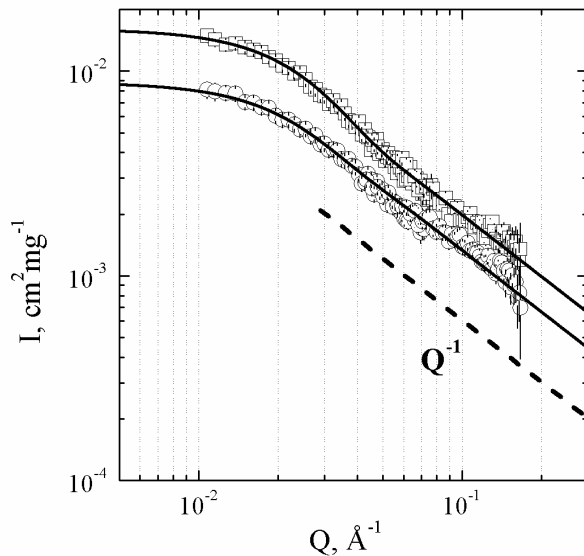
The values for the length and radius obtained for the pHtrII-cyt molecules in dPBS buffer were $L_{\text{PBS}} = 202 \pm 5 \text{ \AA}$ and $r_{\text{PBS}} = 7.2 \pm 0.3 \text{ \AA}$, respectively. From these values, the radius of gyration R_g was calculated based on the cylinder model. For a cylinder of length L , radius r and unifrom mass distribution, R_g is given by:

$$R_g^2 = L^2/12 + H^2/2 \quad (6)$$

For pHtrII-cyt, this gives a radius of gyration of $R_g = 58.5 \text{ \AA}$. This value is similar to the radius of gyration value obtained directly from Eq. 1, which was $50.8 \pm 0.8 \text{ \AA}$. The overall shape of the SANS spectrum measured in dPBS + 4M KCl was essentially identical to that observed in dPBS buffer alone. In contrast, the reduced zero intensity G :

$$G/c = 1/d_p V \Delta\rho^2 \quad (7)$$

in the presence of 4 M KCl in dPBS buffer was 1.8 higher than the zero intensity G observed in dPBS buffer alone. This increase can either result from a change in the particle volume V and/or the square of the scattering contrast. If we assumed a constant volume ($V_{\text{SALT}} = V_{\text{PBS}}$), the scattering length density of HtrII-cyt in D_2O would be $\rho_p = 2.3 \times 10^{10} \text{ cm}^{-2}$. This value would be much lower than expected for proteins in D_2O and could only be accounted for if the protein would bind hundreds of K^+ ions. On the other hand, if we assumed a constant scattering length density ($\rho_p^{\text{SALT}} = \rho_p^{\text{PBS}}$), the particle volume would increase by a factor of 12. Thus, the result indicates that the increase in zero intensity must result from a combined increase in particle volume and change in scattering contrast. In particular, if we assume $V_{\text{SALT}} = 2V_{\text{PBS}}$, the scattering length density of pHtrII-cyt in dPBS + 4 M KCl becomes $\rho_p = 3.22 \times 10^{10} \text{ cm}^{-2}$. This value is very close to the value typically observed for proteins in D_2O . The decrease of the scattering length density from $4.37 \times 10^{10} \text{ cm}^{-2}$ in dPBS to $3.22 \times 10^{10} \text{ cm}^{-2}$ in the presence of 4 M salt suggests exclusion of D_2O from the protein's interior, either by "tightening" of the structure and/or by binding of K^+ ions.



The volumes and scattering length densities from the above calculations were used to approximate the experimental scattering curve by using Eq. 1. The resulting curve is shown in Fig. 1. The molecule length and radius were calculated according to Eq. 4 and 5. The length and radius increased from $L_{\text{PBS}} = 202 \pm 5 \text{ \AA}$ and $r_{\text{PBS}} = 7.2 \pm 0.3 \text{ \AA}$ to $L_{\text{SALT}} = 248 \pm 7 \text{ \AA}$ and $r_{\text{SALT}} = 9.1 \pm 0.4 \text{ \AA}$. When calculating the radii of gyration using these values and comparing them to the direct calculation using Eq. 1, a significant difference between $R_g = 56 \pm 1 \text{ \AA}$ (obtained from Eq. 1) and $R_g = 72 \text{ \AA}$ (calculated from Eq. 6) was observed. Since the experimental value is less than the theoretical value, the mass is either concentrated at the center of the cylinder or the cylinder is not ideal, i.e. the diameter at the center is larger than that on the edges. Thus, there is non-homogeneous mass distribution within the pHtrII-cyt dimer molecule in the presence of 4 M KCl in contrast to the pHtrII-cyt monomer in dPBS alone, which displayed uniform mass distribution.



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

Proposal number:	KW1-04-069		
Experiment title:	Aggregation behaviour of disk-like porphyrin trimers.		
Dates of experiment:	11-13 March 2005	Date of report:	6 October 2005
Experimental team: Names	Addresses		
Van Hameren, Richard Feiters, Martin Elemans, Hans Rowan, Alan Nolte, Roeland	Institute for Molecules and Materials Radboud Universiteit Nijmegen Toernooiveld 1 6525 ED Nijmegen The Netherlands		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

Experimental report text body

Our group has recently demonstrated that porphyrin hexamers and dodecamers can form ring-shaped aggregates at the solid-liquid interface. ^[1-3] Previous SANS measurements have demonstrated that the porphyrin hexamers self-assemble into cylindrical-shaped aggregates in deuterated chloroform (CDCl₃). ^[4] We have designed and synthesized a disk-shaped porphyrin trimer (TAP, Figure 1A), which upon dissolution in CDCl₃ aggregates into columnar stacks, as established by NMR. The aggregation is governed by π - π stacking of aromatic surfaces of the porphyrins in combination with the formation of an intermolecular hydrogen bonding network between the amide functions of neighbouring molecules. Finally, the molecule is appended with long alkyl tails which enhance the solubility.

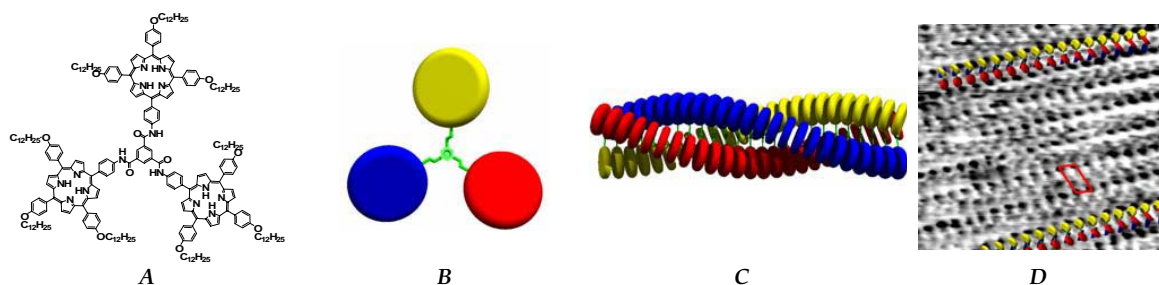


Figure 1. Chemical structure (A) and schematic representation (B) of TAP, which self-assembles into columnar stacks (C). At the solid-liquid interface, the columnar stacking of TAP was confirmed by STM (D): scan size = 21 x 24 nm², V_{bias} = - 369 mV, I_{set} = 1.0 pA.

The performed SANS measurements clearly demonstrated that in both CDCl_3 and deuterated toluene (toluene- d_8), TAP self-assembles into cylindrical-shaped particles (Figure 2). It must be stated that TAP gels the CDCl_3 at the applied concentrations and therefore the long alkyl tails are expected to be (almost) fully stretched. Taking this into account, the diameter of the cylindrical particles corresponds in both solvent systems to the diameter of one molecule. The different stacking behaviour can also be seen in the average length of a stack; the obtained length in CDCl_3 (47 nm) is 9 times longer than the length in toluene- d_8 (5.3 nm). This can be explained by the interference of the aromatic toluene- d_8 solvent molecules with the π - π stacking of TAP, which decreases the supramolecular interactions, resulting in smaller stacks.

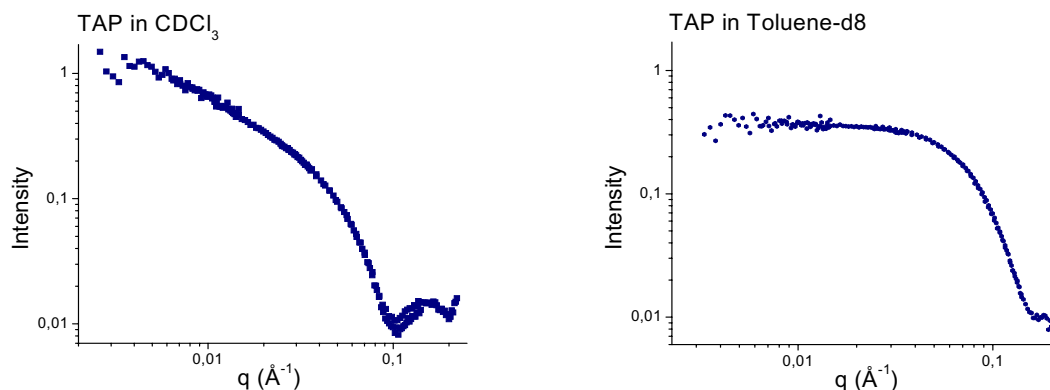


Figure 2. SANS measurements in CDCl_3 and toluene- d_8 at 293 K, at concentrations of 15,0 g/l and 15,3 g/l respectively. Both demonstrate the presence of cylindrical aggregates, however, the difference in length of the stacks is substantial.

Secondly, the influence of the temperature and the concentration on the length of the self-assembled stacks was investigated. The SANS experiments in CDCl_3 showed that the length of the aggregates decreases with temperature and increases with concentration.

The SANS measurements in toluene- d_8 demonstrated less predictable phenomena. Increasing the temperature from 293 to 343 K did not significantly change the average length of the aggregates (Figure 3). Remarkably, an increase in concentration decreases the average length slightly. On the contrary, the diameter slightly increases at a higher concentration, resulting in an almost constant volume of an average stack and thus the number of molecules in one stack remains constant. Apparently, increasing the concentration in toluene- d_8 leads only to an increase in the number of stacks, but not to an increase in the average length of the aggregates of TAP.

The change in the length-diameter ratio might be a property of the stack, but might also be an artefact as a result of experimental and fitting errors. Therefore, no conclusions can be drawn concerning this observation.

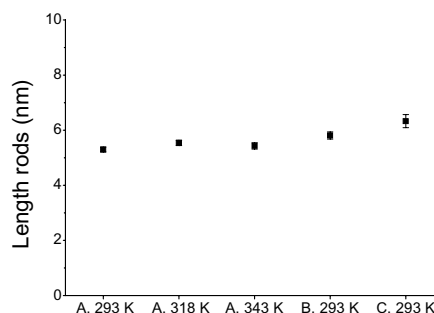


Figure 3. The average length of a columnar stack of concentration (A: = 15,0 g/l; B: = 7,4 g/l; C = 3,7g/l) and temperature (Kelvin).

- [1] J. A. A. W. Elemans, et al. *Adv. Mater.*, **2003**, 15, 2070.
- [2] M. C. Lensen et al. *Chem. Commun.*, **2004**, 762.
- [3] M.C. Lensen et al. *Chem-Eur. J.*, **2004**, 10, 831.
- [4] M. C. Lensen et al. *Experimental reports 2004*, Forschungszentrum Jülich GmbH, **2005**, 280.



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

Proposal number:	KW1-04-070		
Experiment title:	Change of heterogeneities with deformation: focus on low deformation		
Dates of experiment:	01/2006	Date of report:	31/05/06
Experimental team: Names	Addresses		
CASAS Frédéric ABA-SIMIONESCO Christiane	Laboratoire de Chimie Physique bat 349 Université Paris Sud 91405 Orsay cedex Laboratoire de Chimie Physique bat 349 Université Paris Sud 91405 Orsay cedex		
MONTES Hélène LEQUEUX François	ESPCI, UMR 7615, 10 Rue Vauquelin 75005 PARIS ESPCI, UMR 7615, 10 Rue Vauquelin 75005 PARIS		
Local Contact:	Henrich Frielinghauss		

Experimental report text body

A polymer can be stretched and several studies have shown that heterogeneities are created during stretching^[1-3]. Since a glassy polymer is an out-of-equilibrium thermo-dynamical state in which disorder or intern stress can be trapped, many works explain that the disorder increases as it undergoes an inelastic deformation; for instance, Oleinik speaks about micro-domains which are created and grow^[1]. On one hand, a cold drawn polymer is considered as strongly heterogeneous at all scales involved at the different stages of the deformation. First strong density fluctuations are observed at local scales (A-B Fig 1). Beyond the yield point (B), conformation changes of the polymer chains appear leading to orientation fluctuations (B-C figure 1)^[3] (10 nm).

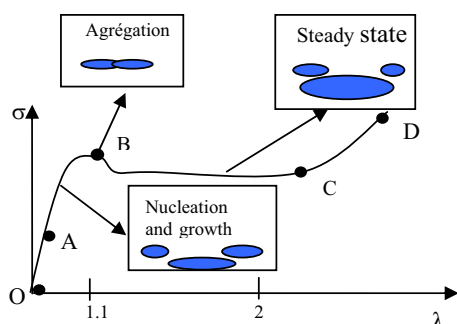


Figure 1 : Representation of creation of heterogeneities during deformation process. This process was proposed by Oleinik^[1].

The aim is to observe the influence of different deformations on low deformations. We want to study particularly the influence of λ because, as shown in Figure 1, for small λ , PMMA must be heterogeneous and when the deformation become larger, we reach the plastic domain where it is possible that the sample has reached a homogeneous state with aggregated defects. So, we performed SANS measurements on glassy PMMA samples stretched at different deformation on a q range from $0.002 \text{ \AA}^{-1}$ and $0.15 \text{ \AA}^{-1}$ (KWS1). Measurements were done on samples composed of 90% of crosslinked protonated PMMA chains. We compare the structure of the PMMA stretched chains. This experiment is the continuity of a precedent proposal (KW3-04-002).

A part of the results of our experiment are represented in the figures 2a, 2b and 3a, 3b for PMMA stretched at 94°C and $V=0.002\text{mm/s}$ for two deformations; $\lambda=1.15$ and $\lambda=1.4$. The results show no particular length scale appears for small deformation ($\lambda=1.15$). For higher deformation ($\lambda=1.4$), we observed a non affine deformation which occurs in the plastic domain and which was observed in for deformation of $\lambda=2$. So, no lengths are characteristic of the disorder associated to low deformation in the q range of the experiment. This experiment need to be completed by more experiments at higher q range because the disorder occurs at smaller length scale.

[1] E.F. Oleinik et al. Polym. Sci **35** 11 (1993) 1819 ; [2] R. Quinson et al. J. Mat. Sci **31** (1996) 4387 ;[3] Hasan O et al J. polym. Sci., PartB, 1993,31,185

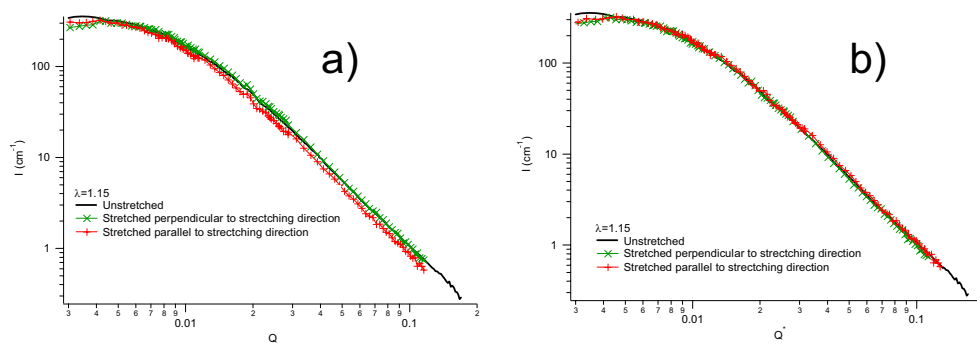


Figure 2 : a) SANS measurement of PMMA stretched at 94°C , $V=0.002\text{mm/s}$ and $\lambda=1.15$. b) Same sample where data were plotted versus the reduced variable q^* that takes into account the affine deformation of chains : perpendicular to the stretching direction $q^*=q/\sqrt{\lambda}$, parallel to the stretching direction $q^*=q \times \lambda$.

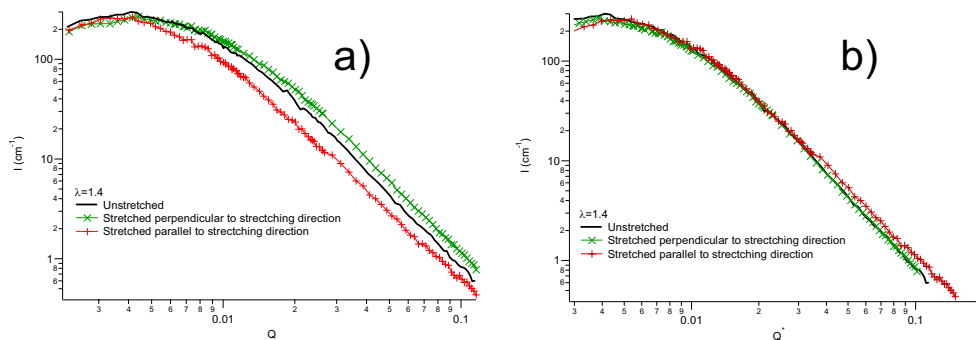


Figure 3 : a) SANS measurement of PMMA stretched at 94°C , $V=0.002\text{mm/s}$ and $\lambda=1.4$. b) Same sample where data were plotted versus the reduced variable q^* that takes into account the affine deformation of chains : perpendicular to the stretching direction $q^*=q/\sqrt{\lambda}$, parallel to the stretching direction $q^*=q \times \lambda$.



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

Proposal number:	KW1-04-071		
Experiment title:	Effects of different salts on aggregation features of β -lactoglobulin		
Dates of experiment:	18.05. – 22.05.2006	Date of report:	09.06.2006
Experimental team: Names	Addresses		
Raffaele Sinibaldi Maria Grazia Ortore Francesco Spinozzi Paolo Mariani Flavio Carsughi	Dipartimento di Scienze Applicate ai Sistemi Complessi, Università Politecnica delle Marche, Via Brece Bianche, 60131 Ancona, Italy Forschungszentrum Jülich, D-52425 Jülich		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

Experimental report text body

β -lactoglobulin (β LG) is the major whey protein found in the milk of bovine and other ruminants. It is an acidic stable protein which exists at the normal pH of bovine milk as a dimer consisting of two monomeric subunits with a molecular weight of 18350 Da (162 residues). β LG assumes a monomeric native structure at pH 2.3 in the absence of salt, and the dimeric structure is stabilized increasing the ionic strength of the solution. We have already studied the structural properties of β LG in acidic solutions (pH 2.3), evidencing the presence of a monomer-dimer equilibrium affected by the ionic strength, obtained with NaCl [3].

In order to derive the factors which control the BLG stability and interactions, we have compared the effects of NaCl to other different salts, which will be chosen according to the Hoffmeister series. In particular, at acidic pH in aqueous solutions containing NaH_2PO_4 , NaClO_4 and NaSCN (i.e., from stabilizing kosmotropes to disruptive chaotropes). Literature data show that the mechanism of the anions binding is dependent by their chaotropic effects [5]: sedimentation equilibrium analysis of β LG in the presence of various concentration of different kind of salts has confirmed that the order of the effectiveness of various anions follows the electroselectivity series. In particular, multivalent anions have been demonstrated to be more effective than monovalent ones, and among them chaotropic anions more effective than kosmotropic ones. Such differences cannot be simply explained, first of all because the Debye-Huckel screening effect of salts is independent of anion species. In BLG, we observed that when the NaCl raises the surface free energy of the protein, protein-protein attraction increases, leading to a process of dimerization [4]. However, on lysozyme and ovalbumin [6] it has been shown that if the surface chemistry of proteins is altered by binding of a specific ion, salting-in is observed when the interactions between (kosmotrope) ion-protein complexes are more repulsive than those between the uncomplexed proteins, while salting-out is observed when interactions between (chaotrope) ion-protein complexes are more attractive than those of the uncomplexed proteins.

Moreover, the thermodynamic characterisation of the process of β LG dimerization in different salts confirmed the dominant role of the hydrophobic effects [5], revealing at different temperature small differences from the kind of salt present in solution. We have performed SANS experiments on β LG dilute solution (8 mg/ml) in water with different salts and in fully deuterated conditions. The experimental landscape (Fig.1 and Fig. 2) clearly confirms the order of the effectiveness of different anions following the Hoffmeister series.

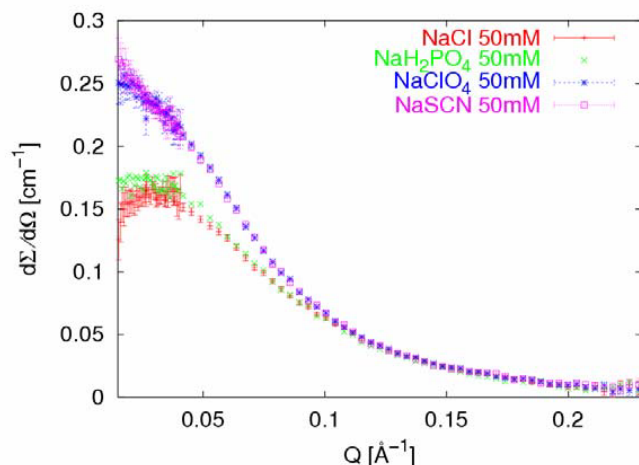


Fig.1 Differential Cross Sections relative to BLG solutions containing the same ionic strength (50mM) obtained with different salts.

More precisely, data concerning β LG dissolved at the ionic strength of 50mM show that the dimerization process has been induced by chaotropic anions in a more efficiently way. The β LG monomer fraction increases from 67% (NaCl) to 98% (NaSCN), as resulting from the fitting procedure.

The same trend has been reproduced at the highest ionic strength (100mM): in this condition the chaotropic anions induce the formation of bigger aggregates, whose contribution in the form factor hides structure factor modifications. The

experimental landscape confirm literature's suggestion about the different anion effectiveness on β LG monomer-dimer equilibria.

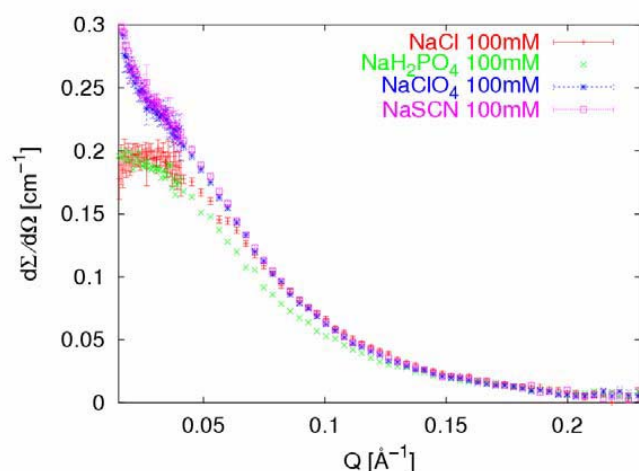


Fig.2 Differential Cross Sections relative to BLG solutions containing the same ionic strength (100mM) obtained with different salts.

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

Proposal number:	KW1-04-072		
Experiment title:	Heterogeneous polymer micelles and their interactions with proteins		
Dates of experiment:	1.3-4.3/2005 at KW1 4.3-8.3/2005 at KW3	Date of report:	25.12.05
Experimental team: Names	Addresses		
BIANCO-PELED, Havazelet	Department of Chemical Engineering, Technion, Haifa, ISRAEL 32000		
SHAMAI, Keren			
BITTON, Ronit			
Local Contact:	Dr. Aurel Radulescu		

Experimental report text body

Background

The use of polymer brushes as surface modifiers has been recently shown to be a very promising way of manipulating the interaction of surfaces with proteins[1]. For example, hydrophilic polymer brush has been shown to be the most effective method to prevent adsorption of proteins. Contrary, other polymers are known to be attractive to proteins. In the preformed experiments we examined whether it is possible to control the adsorption of proteins to a colloid particle by using a “heterogeneous polymer brushes” (HPB). To the best of our knowledge, no one has experimentally attended that question yet.

Objectives

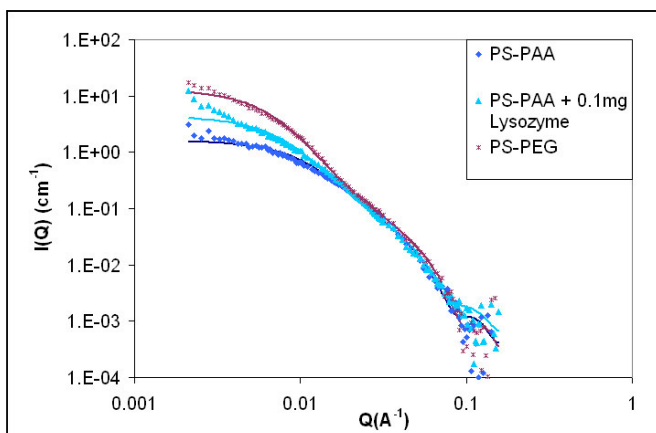
The objectives of this project are to study the HPB created *via* self-assembly of a mixture of neutral (polystyrene-*b*-Polyethylene glycol) (PS₃₄-PEG₃₇₇) and charged (polystyrene-*b*-polyacrylic acid) (PS₃₂-PAA₂₇₇) diblock copolymers. And to examine the relations between the composition of the micelles and their protein binding properties using Lysozyme (a ~2nm negatively charged protein) as a model.

Experimental

Since PS-PAA is not soluble in aqueous media, the block copolymers were first dissolved in Tetrahydrofuran (THF) which is a common solvent for both the hydrophobic (PS) and hydrophilic (PEG, PAA) blocks. Then, addition of water, a selective precipitant of the PS block, induces micelles formation. Homogeneous brushes were constructed for each block copolymer at different concentrations (1mg/ml, 3mg/ml) and heterogeneous brushes were constructed from 3mg/ml binary mixtures at different compositions (S1-10%, S2-25%, S3-50%, S4-75%, S5-90% PS-PAA). Scattering curves were measured on the KWS1 instrument with and without addition of proteins. Few of the samples were measured on the KWS3 as well.

Results

Our first experiments involved 1mg/ml PS-PAA micelles and 1mg/ml PS-PEG micelles (fig 1). The scattering curves were fitted to theoretical model of micelles with a spherical core (R) and Gaussian polymer chains (R_g) attached to the surface, where N_c is the number of chains in each micelle [2].

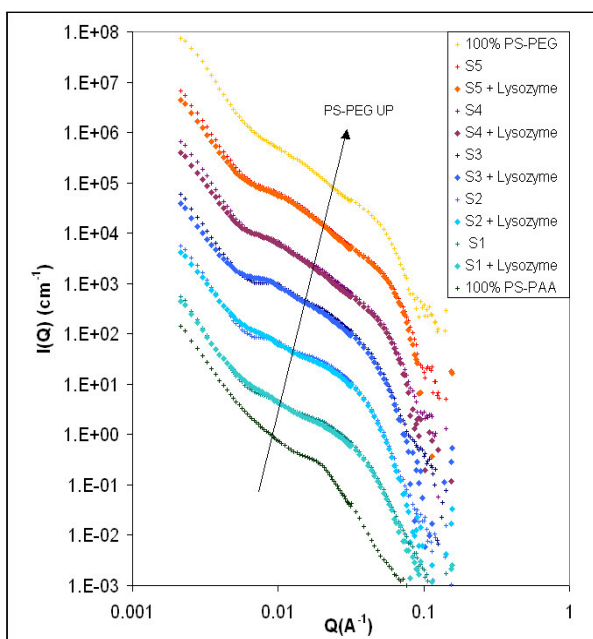


	R (Å)	R _g (Å)	N _c
PS-PAA	50	101	23
PS-PAA + 0.1 mg lysozyme	50	139	23
PS-PEG	45	154	62

Fig 1: Scattering curves for (♦) 1mg/ml PS-PAA micelles (Δ) 1mg/ml PS-PAA micelles with 0.1 mg/ml of Lysozyme (x) 1mg/ml PS-PAA micelles. The solid lines represent the curves fit to theoretical model of spherical block copolymer micelles (1).

As can be seen after addition of protein to the PS-PAA sample there is an increase in the shell dimension R_g, which may suggest protein adsorption on the micelles. Additionally, a 60% increase in the shell electron density was observed. The “excess” scattering at the low angles might be due to the presence of a second population of larger objects. The scattering from PS-PEG micelles with added lysozyme was not measured since PEG is commonly used polymer for prevention of protein adsorption on biomaterials surfaces [3].

In the second part of our experiment, we measured the scattering from the homogeneous and the heterogeneous micelles at 3mg/ml before and after the protein addition (fig 2). The two distinct slopes, observed in all scattering curves, suggest a bimodal size distribution. Using Guinier approximation and the position of the



maxima at about 0.02 Å⁻¹, values of R_g~3000Å and R_g~300Å were calculated for the large and the small particles. The size of the larger particles was obtained from further measurements at the KWS-3 instrument. A simple mathematical analysis have shown that the scattering curves of the heterogeneous micelles is not a superposition of its two homogeneous curves. Therefore we concluded that mixed micelles were obtained. A comparison between the scattering curves before and after the protein addition revealed changes in the peak position. These differences are believed to result from protein adsorption and seems much more significant at 50% and 75% of PS-PAA block. A higher percentage of PS-PAA does not increase the protein adsorption. This may be due to an optimal composition for protein adsorption.

Fig 2: Scattering curves from homogeneous and heterogeneous micelles 3mg/ml before (+) and after (♦) Lysozyme addition.

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

Proposal number:	KW1-04-073		
Experiment title:	Complex Coacervate Core Janus Micelles		
Dates of experiment:	11-13 April 2005	Date of report:	21 December 2005
Experimental team: Names	Addresses		
Hellweg, Thomas	TU Berlin STRANSKI LABORATORIUM Skr. ER1 Strasse des 17.Juni 112 10623 BERLIN, Germany Laboratory of Physical Chemistry and Colloid Science Wageningen University P.O. Box 8038 6700 EK Wageningen, Netherlands		
Barneveld, Peter			
Voets, Ilja			
Hofs, Bas			
Local Contact:	Dietmar Schwahn		

Experimental report text body

Janus micelles (micelles with a micro-phase separated corona) have generated substantial research interest in modern polymer and colloid science. So far, the existence of reversible Janus micelles has not been reported. This research work aims to study the coronal structure of reversible complex coacervate core micelles (figure 1), spontaneously formed through a combination of associative and segregative micro phase separation, simply by mixing two aqueous diblock copolymer solutions.

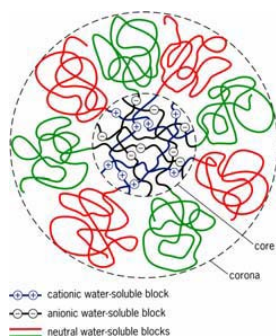


Figure 1: Schematic representation of a Complex Coacervate Core Janus Micelle, indicating the complex coacervate core formed by the polyelectrolyte blocks and the micro-phase separated corona.

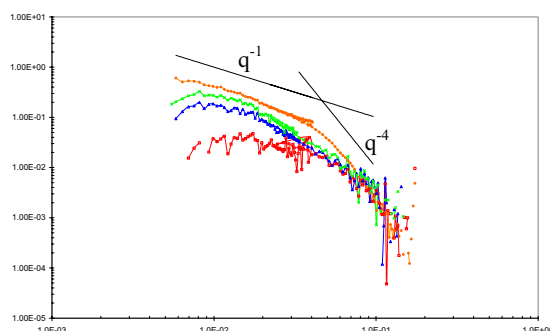


Figure 2: Contrast series for micelles consisting of PAA⁴²-PAAm⁴¹⁷ and P₂MVP⁴⁴-dPEO³⁰⁰ (10g/l, 1mM NaNO₃, pH=5.5, 25°C) for 29% (green), 36% (blue), 54% (red) and 100% D₂O (orange).

We have applied contrast variation as a tool to study corona structure and we have investigated the effect of temperature as a switch between Janus and non-Janus type.

As the scattering curves at different temperatures up to 80°C in pure D₂O superimpose onto one single master curve, we conclude that temperature is not substantially changing the (corona) structure of the micelles.

A typical contrast series for the highest concentration is presented in figure 2. Interpretation of these series in terms of coronal structure (through contrast calculations and form factor/ R_g fits for various micellar morphologies and coronal structure) is in progress.



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

Proposal number:	KW1-04-076		
Experiment title:	Investigation of the gel structures from mixtures of chitosan and fibrinogen		
Dates of experiment:	7 to 9-March-2005	Date of report:	15-Feb-2006
Experimental team: Names	Addresses:		
Yuan Wang Dong Qiu 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

(Please use 12 pt letters here !)

Chitosan is the N-deacetylated derivative of chitin, a naturally abundant polysaccharide found in the exoskeleton of shellfish like shrimps or crabs. [1] Gelatin is another natural polymer, which is obtained by thermal denaturation or physical and chemical degradation of collagen. [2] Due to their biocompatibility, low toxicity, biodegradability and adhesiveness, the blends of chitosan and gelatin have been largely studied for potential uses in pharmaceutical fields [3], tissue engineering and wound dressing [4]. In this project, we studied the structure of the composite solution of chitosan, gelatin and a polyelectrolyte, polystyrene sulfonate sodium (PSSNa).

Macromolecules may form structures on different length scales in solution [5]. De Gennes [6] predicted that the pair correlation function for a polymer in a good solvent follows the Ornstein-Zernike law, which has a Lorentzian form in Q-space

$$I(Q) = \frac{I(0)}{1 + Q^2 \xi^2} \quad (1)$$

where ξ is the average correlation length and $I(0)$ is the fitted scattering intensity at zero Q. For large scale inhomogeneity, an adaptation [7] of the Debye-Bueche equation [8] was used which is given by

$$I(Q) = \frac{I(0)}{(1 + Q^2 a^2)^2} \quad (2)$$

where a is the average inhomogeneity length. Therefore, we can see that at different Q-ranges, scattering from different length scale structure dominate. The results are summarized in Table 1. The concentration of PSSNa is fixed in this study.

It is shown that these polymers can be mixed evenly. The correlation length decreases with the increase of gelatin content, however, when no chitosan is present, the correlation length increases again, which suggests a complex interaction between polystyrene sulfonate and gelatin and the important role played chitosan. The large scale structure size decreases monotonically with the gelatin content, which is in good agreement with the rheological measurements. This suggests that the rheological behavior is mainly determined by the large scale inhomogeneity length. A detailed analysis is in progress.

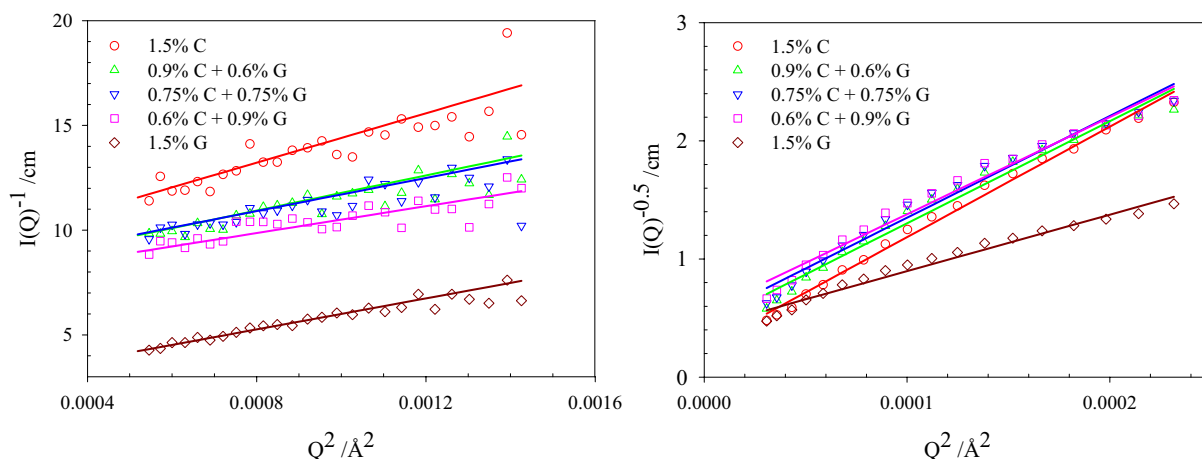


Figure 1. Fits of scattering from mixtures of chitosan, gelatin to the Lorentzian model (left) and Debye-Bueche model (right).

Table 1. Parameters obtained from the fits in Figure 1.

Chitosan Weight Fraction	1	0.6	0.5	0.4	0
Inhomogeneity Length ($\text{\AA}$)	193.7	140.6	132.7	121.7	106.8
Correlation Length ($\text{\AA}$)	26.3	23.5	22.6	20.9	40.1

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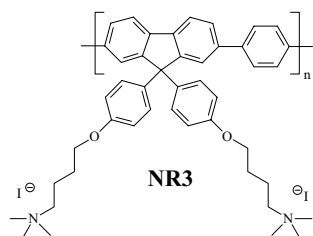


Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

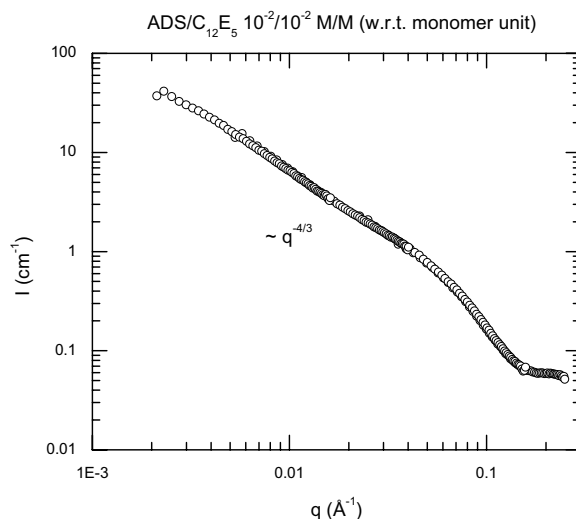
Proposal number:	KW1-04-077		
Experiment title:	Structural studies on aggregates formed between nonionic surfactants and water soluble fluorene copolymers		
Dates of experiment:	6-7 April and 13-14 June 2005	Date of report:	3/12/05
Experimental team: Names	Addresses		
Hugh D. Burrows	Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal		
Matti Knaapila	OEM Research Group, Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK		
Local Contact:	Dr Wim Pyckhout-Hintzen		

Experimental report text body

Conjugated polyelectrolytes are finding increasing applications as sensors for chemical and biological systems.^{1,2} However, they tend to aggregate and have low solubility in aqueous solutions, such that organic cosolvents are normally needed to dissolve them, limiting their application in the sensing of biological systems such as nucleic acids. We have recently suggested, based on the results of fluorescence measurements, that nonionic surfactants, such as pentaethyleneglycol monododecyl ether ($C_{12}E_5$), can break up these aggregates and incorporate these polymers in long, cylindrical micelles.² However, proof of this was missing. The objective of these small angle neutron scattering (SANS) measurements was to obtain structural information on the species formed with the cationic conjugated polyelectrolytes poly{9,9-bis[6-(N,N-dimethylamino)hexyl]fluorene-co-1,4-phenylene} iodide (NR3), and a commercial equivalent (ADS181), in the presence of $C_{12}E_5$ in aqueous (D_2O) solutions. The structure of NR3 is given below.



SANS studies were carried out on $C_{12}E_5$ solutions in D_2O (1 – 10 mM) alone, and with varying concentrations of either NR3 or ADS181 (up to 10 mM in terms of monomer units). These were corrected for transmission, background, sample cell, and detector efficiency. Typical data as a log-log plot for 10 mM ADS181 in $C_{12}E_5$ (10 mM) / D_2O solution is shown below.



Control SANS experiments were made with the polymer NR3 in perdeuterobenzene and D_2O solutions. The SANS results support the idea that the surfactant breaks up aggregates of the conjugated polyelectrolytes, and indicate that in the presence of $C_{12}E_5$, NR3 or ADS181 are present in similar wormlike micelles to those observed with the pure surfactant. The results are in agreement with NMR studies on these systems. However, the SANS data suggest that the fairly rigid polymers induce more ordered segments into the surfactant aggregates. Detailed analysis and modelling of the data is in progress, and is being combined with dynamic light scattering studies.

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

Proposal number:	KW1-04-078		
Experiment title:	Quantitative relationship between non linear mechanical properties and particle arrangement in model filled elastomers.		
Dates of experiment:	February 2005 (2 days)	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 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 (C8TES) in order to perform a weak inter action and Methacryloxypropyltrimethoxysilane (TPM) for the covalent bonding.

The so-filled elastomers were prepared using Ford method¹, consisting in grafting the particle directly and transfer it to the monomer using dialysis. Suspensions were then adjusted to the write 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. 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.

We have characterized for each graft three different sizes of silica particles: from 30 nm to 100 nm, using three typical concentration of 0.09, 0.13 and 0.16 in volume fraction.

The results showed that for strong interacting particles (TPM graft), all size and concentration leads to very well dispersed states (fig. 1).

Whereas for weaker interaction only the SANS measurements leads to the aggregation of the particles whatever the size or the concentration of the particles (fig. 2). Measurements done on the initial suspension of C8TES-grafted silica show that the particles are very well dispersed in the monomer media. This let us think that aggregation occurs during the polymerization step and can be due to depletion.

Therefore we decided to work on the polymerization step, we think that using temperature can have some effect on the final dispersion. Heating the sample during polymerization may bring enough energy to the particles to deaggregate them, whereas cooling down the system to 0°C or -20°C may freeze the system in a good

dispersion state. We also wanted to modify the interaction between the silica particle and the poly(ethyl acrylate) matrix using graft such as: Acetoxyethyltrimethylchlorosilane (MCSNC) to perform some hydrogen bonding and Hexamethyldisilazane (HMDS) to get some weak interaction.

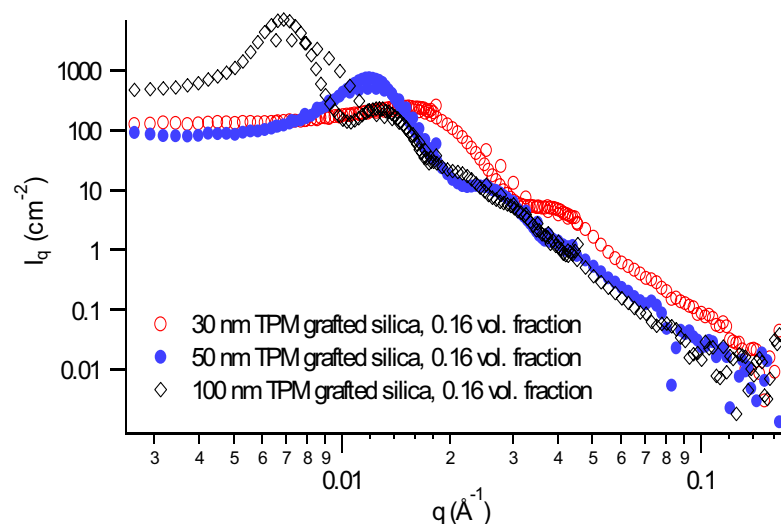


Fig.1 TPM grafted silica particles, 30 nm (red), 50 nm(blue) and 100 nm (red)

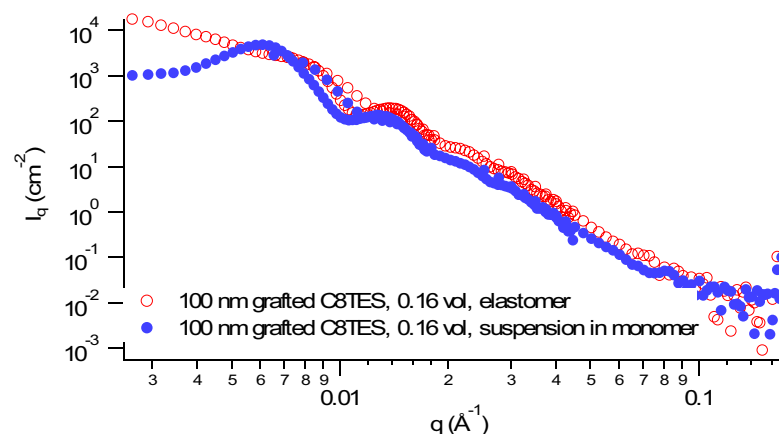


Fig.2 100 nm grafted silica particles, dispersion in poly(ethyl acrylate) matrix in red, and ethylacrylate monomer in blue



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

Proposal number:	KW1-04-081		
Experiment title:	Hierarchical structure of silica and Carbon Black 1		
Dates of experiment:	29.01. – 30.01.2005	Date of report:	01.06.2006
Experimental team:			
Names	Addresses		
G. J. Schneider V. Vollnhals D. Göritz	Institut für Physik Universität Regensburg 93040 Regensburg Gerald.schneider@physik.uni-regensburg.de		
W. Pyckhout-Hintzen	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Dr. W. Pyckhout-Hintzen		

Experimental report text body

1. Abstract

Carbon Blacks are important fillers used for improving many of the properties of elastomeric materials. The characteristics obtained depend on the structure of the filler and its specific surface, and therefore on its bonding with the rubbery matrix. However the reinforcement mechanism is still not understood to any great extent. Therefore the structure of different commercially produced carbon black samples shall be investigated by means of small angle neutron scattering. By measuring the scattered intensity as a function of scattering length the size and the surface roughness of the aggregates and its spatial arrangement can be determined.

2. Introduction

Dispersing carbon black in rubber improves mechanical properties such as the elastic modulus, tensile strength and abrasion resistance. The effects due to different active fillers are influenced both by the specific inner surface and by the hierarchical structure of the filler. Due to these facts the commercially produced carbon blacks are classified by an industrial norm [1]. Each code starts with a letter describing the processing technique. Concerning the present work carbon-black samples produced with furnace method will be investigated, i.e. the starting letter is N. Afterwards, a number of the form XYZ, describing the structure of carbon black with regard to the reinforcement properties, follows. X is a measurement of the mean diameter of the aggregates and YZ reflects its spatial arrangement. Although not classified by the norm, Maier showed the dependence of the mechanical properties of carbon black filled rubber from the adsorption of polymer chains at the surface of the aggregates [2]. In addition Niedermeier et. al demonstrated the linkage to the surface roughness of the aggregates by computer simulations [3]. By measuring the scattered intensity as a function of scattering length q ($q = 4\pi/\lambda \sin(\theta/2)$), and plotting the result in a log-log-plot, the slope is a function of the roughness of the aggregates, or to be more precise the surface fractal dimension.

Additionally with the same experiment the size of the aggregates and its spatial distribution can be determined. In the present work the series N 110 up to N 990 will be investigated. According to the norm the mean diameter of these carbon black samples vary from 10 nm to 250 nm [1]. These structure sizes can be easily covered by using KWS 1.

3. Results

Figure 1 shows scattering diagrams, i.e. the intensity as a function of the scattering length, for the different samples. For the purpose of a better comparison the intensity values are normalized, therefore the intensity is in arbitrary units. Considering first the q -values larger than 0.2 nm^{-1} the almost identical slopes are evident. For values smaller than $q = 0.2 \text{ nm}^{-1}$ each curve shows a crossover to a second slope. As can be shown the crossover reflects the diameter of the aggregates and the slope at small length scales its spatial distribution. From N 110 to N 990 the crossovers shift to a lower scattering length, i.e. to a higher length scale. The slope at small length scales increases starting from N 110 to N 990.

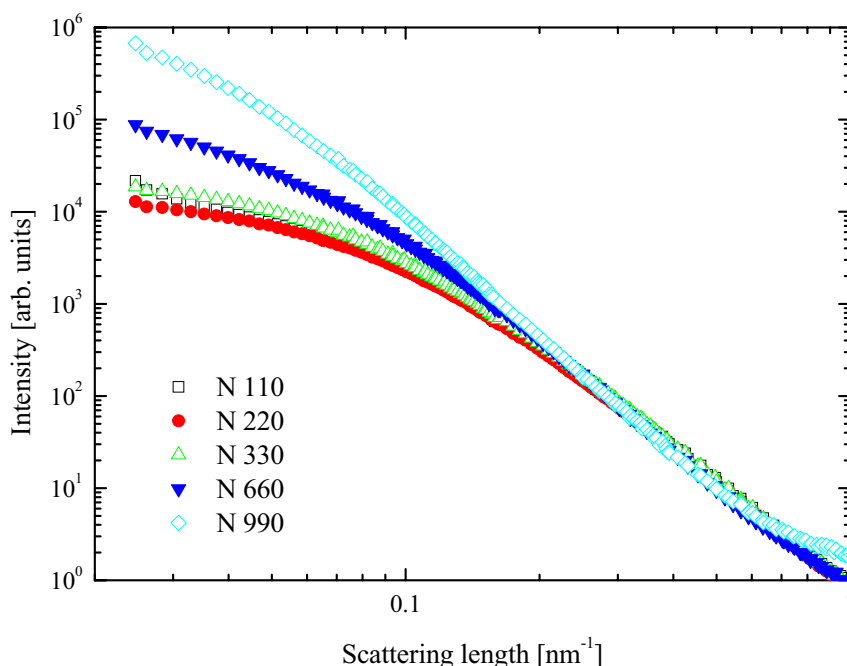


Figure 1: Intensity as a function of scattering length for different carbon black samples.

4. Discussion

The results should only be discussed qualitatively. The shifting of the crossover is in concordance with the norm, but the slopes at small length scales do not reflect the norm. However closest attention should be paid to the surface roughness. Since the slopes are almost identical no change in the surface roughness is expected for the different samples. Therefore the adsorption behavior should not change for the different fillers, and therefore the mechanical properties should not differ.

4. Conclusion

The use of KWS 1 to investigate the structure of carbon black samples was shown. Especially the surface roughness of different samples was shown to be equal.

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

Proposal number:	KW1-04-082		
Experiment title:	Solution properties of inorganic diblock-copolymer micelle complexes for nanodot arrays		
Dates of experiment:	26.01.05-29.01.05	Date of report:	24.03.06
Experimental team: Names	Addresses		
Karthäuser, Silvia	Forschungszentrum Jülich GmbH IFF; Elektronische Materialien		
Rathgeber, Silke			
Kronholz, Stephan			
Local Contact:			

Experimental report text body

An A-B diblock copolymer consists of two chemically different, covalently bonded macromolecular chains. If these exhibit different solubilities, micelles are formed in appropriately chosen solvents. In a non polar solvent for example the non polar chain segment is dissolved while the polar chain segment is insoluble and tends to form the core of a micelle. According to the chemical and physical interactions characterizing the monomer units, the micelles can bind other components, for example leading to complexation or binding of a transition metal compound. In our case the micelle cores are loaded with a transition metal salt (HAuCl_4) which can be reduced to metal nanoparticles.

Dilute solutions of loaded micelles can be used to prepare a thin self-assembled film on a flat substrate. The film is created by dipping the substrate into the micellar solution and pulling it out again at a controlled velocity. If the conditions are chosen appropriately a micellar monofilm is built after evaporation of the solvent. Subsequent plasma treatment can be used to remove the polymer, which means that only small metal nanoparticles are left on the substrate. The location and order of the particles corresponds to the quasi-hexagonal pattern of the closely packed micelles in the original film. This rather regular pattern can serve as template for the building up of nanodot arrays instead of using e-beam lithographic methods with the advantage of easy achievable nanometer sizes with low costs. Our aim was to investigate the correlation between the micellar structure in solution and the resulting arrangement on the substrate after deposition.

In our SANS experiment we wanted to complete our measurements including experiments on the solution properties of the unloaded micellar solutions built from the two different blockcopolymers, (Poly2) and the more asymmetric diblock-copolymer (Poly1). Furthermore our aim was to complete our data set on Poly1 for the same amounts of gold load as measured for Poly2.

In the SANS experiment we have measured the solution properties of unloaded micelles with both fixed block length ratios (Poly1 and Poly2) and micelles built up by Poly1 with varying amounts of gold load. Concentrations have been varied between those relevant for film preparation down to dilute solutions to obtain the form factor yielding information about the structure of a single micelle. The form factors of gold loaded micelles ($L=0.2$ and $L=0.5$) built up from Poly2 are shown in figure 1. As a reference the data obtained for the unloaded micelles ($L=0$) are also included. From these form factors the density profiles for the PVP core, the PS shell and the Au distribution were calculated by a simultaneous core-shell model fit. Figure 2 shows a comparison between Poly1 and Poly2 with the same gold load.

We compared the micelle dimensions and the average inter-micelle spacing in solutions with those obtained from dried monofilms. Obviously the inter-micelle spacing in the dried film is much smaller than the micelle dimension in solution and approaches the dimension of a fully collapsed micelle in case the dipping process is performed slow enough. Currently a publication containing these results is ready to be submitted.

References:

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- [3] O. Glatter, J. Appl. Cryst. **10**, 415 (1977); J. Appl. Cryst. **14**, 101 (1981).

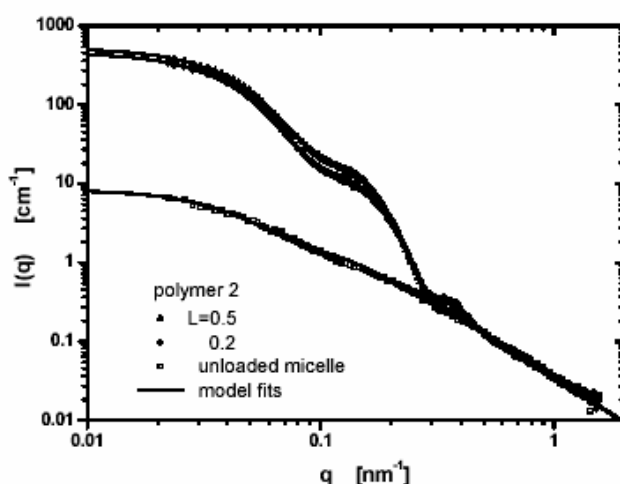


Figure 1:

Form factors obtained for gold loaded micelles (Poly2) with different amounts of Au including the unloaded micelle. The solid lines show the results of the model fit.

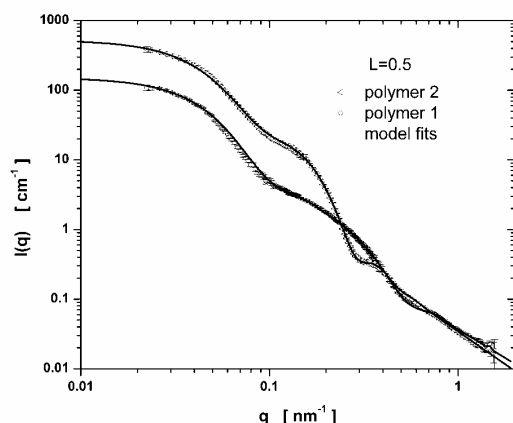


Figure 2:

Form factors for loaded micelles with different block length but same gold load ($L=0.5$). The solid lines show the results of the model fit.



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

Proposal number:	KW1-04-085		
Experiment title:	Micellar properties of PB-PS-PB triblock copolymers in alkanes		
Dates of experiment:	31.01. – 02.02.2005	Date of report:	30/05/2006
Experimental team: Names			
Reidar Lund Lutz Willner Dieter Richter	DIPC, University of Basque Country, Spain Institut für Festkörperforschung, FZJ, Jülich, Germany Institut für Festkörperforschung, FZJ, Jülich, Germany		
Local Contact:	Wim Pychout-Hintzen		

Experimental report text body

In this experimental session, we have investigated the mesoscopic structure of micelles formed by poly(butadiene)-poly(styrene)-poly(butadiene) (PB20-PS20-PB10, the numbers indicate the molecular weight in kg/mole) triblock copolymers immersed in n-hexadecane. The aim was to characterise the micellar properties (aggregation number, core radius etc) with the particular aim to compare the data with previous results obtained on diblock analogue PS10-PB10. The concentration was varied between 0.25- 1 vol.%. No concentration dependent micellization behaviour was found, but the effective forward scattering was observed to decrease with increasing concentration signaturing a repulsive interaction between the micelles.

In order to obtain detailed structural information, the micelles were measured using under three contrast conditions; core contrast (purely deuterated hexadecane), shell contrast (nearly purely hydrogenated hexadecane) and in a average contrast where the interference scattering between the PS and PB parts is visible. The partial form factors including a fit to the core-shell model[1] is shown in figure 1.

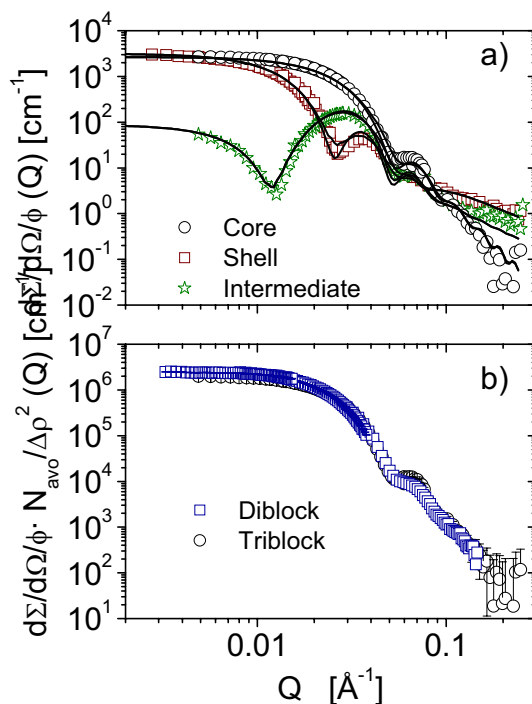


Figure 1. a) Partial form factors of PB10-PS20-PB10 micelles in hexadecane at 20 °C. The solid lines display fit to a core-shell model. b) Comparison between the core scattering of the triblock micelles and the corresponding under core contrast. .

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The data have been fitted with a core-shell model revealing that both the core and the corona can be best fitted with a compact, constant density profile. The aggregation number, P , was found to be approximately 53 chains per micelles which almost perfectly corresponds to the half of the P of the diblock PS10-PB10 micelles which is rather intuitively reasonable as the triblock chain exhibit the double volume compared to the diblock. This is seen directly in the in figure 2 b) where the normalized scattering curves of the cores of both the diblock and triblock micelles are plotted together. Both the forward scattering as well as the minimum coincide very well indicating the same micellar volume and core radius. This is a very important input for the kinetic measurements where we aim to understand the role of chain topology on the exchange kinetics. As both micellar systems has the same size of the core, the kinetic results can bed directly compared.

References:

1. R. Lund, L. Willner, J. Stellbrink, A. Radulescu, and D. Richter, [Macromolecules 37, 9984 \(2004\)](#).



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

Proposal number:	KW1-04-086		
Experiment title:	Study of the formation of silica filler particles obtained from a sol-gel transition inside a rubber.		
Dates of experiment:	24-25/09/2005	Date of report:	28/03/2006
Experimental team:			
Names	Addresses		
Heinrich Martine Pyckhout-Hintzen Wim	IFF Forschungszentrum Jülich		
Local Contact:	Heinrich Martine		

Experimental report text body

This proposal is a part of a study concerning the formation of single, non-agglomerated spherical silica particles from a sol-gel interaction inside a crosslinked network: a PI network swollen in tetraethoxysilan (TEOS, $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$) is immersed in a 2% (w) aqueous solution of ethylamine (EA). The TEOS trapped in the network reacts with the water to produce silica, following the reaction: $(\text{C}_2\text{H}_5\text{O})_4\text{Si} + 2 \text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4 \text{C}_2\text{H}_5\text{OH}$ [1-3]. This method has been used commercially and showed to yield considerably reinforced networks without having to rely on the mixing or processing of both filler particles and polymer chains. This effectively reduces degradation of chains or also the inefficient incorporation of silica in the rubber. The kinetics of the reaction of ortho-silicate with water was not studied in real-time. This SANS investigation should reveal structural details of the process.

In the first part of the study, we have investigated the formation of silica particles in a PI-network ($M_w = 200 \text{ kg.mol}^{-1}$, $M_c = 8 \text{ kg.mol}^{-1}$) directly in the neutron beam, on the q-range $0.01 < q (\text{\AA}^{-1}) < 0.08$ during the 2 first days of the precipitation reaction. The particles radius R obtained in this q-range from Guinier approximations showed that after the 1st hour of reaction and till the 8th hour, particles are progressively growing to reach a size corresponding to $R = 40 \text{ \AA}$, remaining constant till the end of the experiment (= 2 days of reaction). More details are given in experimental report 2004, KW1-04-057.

Knowing the important times of the reaction from this first set of experiments, we have investigated in details the silica formation and aggregation processes in this proposal. For this purpose, we have prepared samples made of PI networks ($M_w = 200 \text{ kg.mol}^{-1}$, $M_c = 100 \text{ kg.mol}^{-1}$) swollen in TEOS, allowed to react with an aqueous solution of EA for limited specific times between 1/2 hour and 1 day. The use of these “quenched”

samples has the advantage that SANS experiments can be performed on the full q -range ($0.002 < q \text{ (}\text{\AA}^{-1}\text{)} < 0.2$) to obtain information at all the available length scales and at different stages of the reaction.

The obtained structure functions $S(q)$ are given on Figure 1, together with the corresponding predictions from the empirical approach for polymeric mass fractals of Beaucage [4]. A 2-level structure is observed with respective radii R_{core} and R_{cluster} and power law exponents P_s and P_{clu} . The radii as a function of the reaction time are plotted on Figure 2, and the fits parameters are summarized in Table 1.

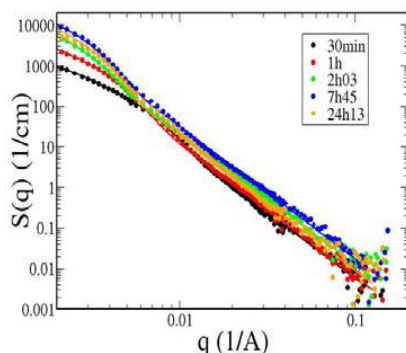


Fig 1: Structure functions for the different reaction times (points for experiment, lines for theory [4]).

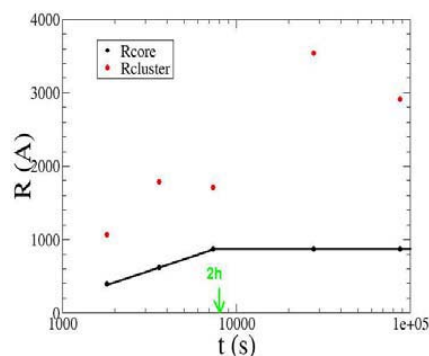


Fig 2: Radii of the 2 structures of the Beaucage model as a function of the reaction time.

Figure 2 and Table 1 show that the radius of the 1st level structure (R_{core}) is increasing during the first 2 hours of the precipitation reaction and afterwards remains constant to a value of about 870 Å. At the same time, the radius of the 2nd level structure (R_{cluster}) seems always to increase. The exponent P_{clu} indicates that different aggregation processes are involved during the reaction (a value of 2.5 is a sign for a diffusion-limited-aggregation process and 1.8 a sign for cluster-cluster aggregation process).

Time	R_{core} (Å)	P_s	R_{cluster} (Å)	P_{clu}
30 min	397	3.3	1071	2.4
1 h	619	3.3	1789	2.2
2 h 03	868	3.3	1710	1.8
7 h 45	868	3.3	3540	1.8
24 h 13	868	3.3	2912	2.9

Table 1: Radii of the 2 structures (R_{core} and R_{cluster}) and power law exponents P_s and P_{clu} .

The preliminary results given here show that SANS is a powerful technique to follow the processes of silica precipitation and aggregation which occur at different times and length scales.

But further experiments and data evaluations are necessary to understand the silica formation process as a function of the obtainment conditions especially how the value of M_c is influencing the primary particle size.

[1] J.E. Mark et al, Polymer Bulletin, **12**,413(1984)

[2] Y. Ning et al., Polymer Bulletin, **13**,155(1985)

[3] C. Jiang et al., Makromol. Chem, **115**, 2609(1984)

[4] G. Beaucage, J.Appl.Crystallography **28**, 717 (1995) ; G. Beaucage, J.Appl.Crystallography **29**, 134 (1996)



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

Proposal number:	KW1-05-001		
Experiment title:	Study of the mechanism of formation of poly(vinylalcohol) hydrogels by freeze/thaw techniques		
Dates of experiment:	16-21 May 2005	Date of report:	5 June 2006
Experimental team: Names	Addresses:		
Finizia Auriemma,	Dipartimento di Chimica, Università di Napoli Federico II, Complesso Monte Sant' Angelo, via Cintia, 80126 Napoli (Italy)		
Roberto Triolo			
Rosa Ricciardi.			
Local Contact:	Vitaly Pipich		

Experimental report text body

The kinetics of sol-gel transition of homogeneous aqueous poly(vinyl alcohol) (PVA) solutions during freezing and thawing cycles has been investigated by SANS experiments. SANS measurements of PVA solutions in heavy water at different polymer concentrations have been performed during consecutive freezing (-13°C) and thawing (20°C) steps, as a function of time (Figure 1).

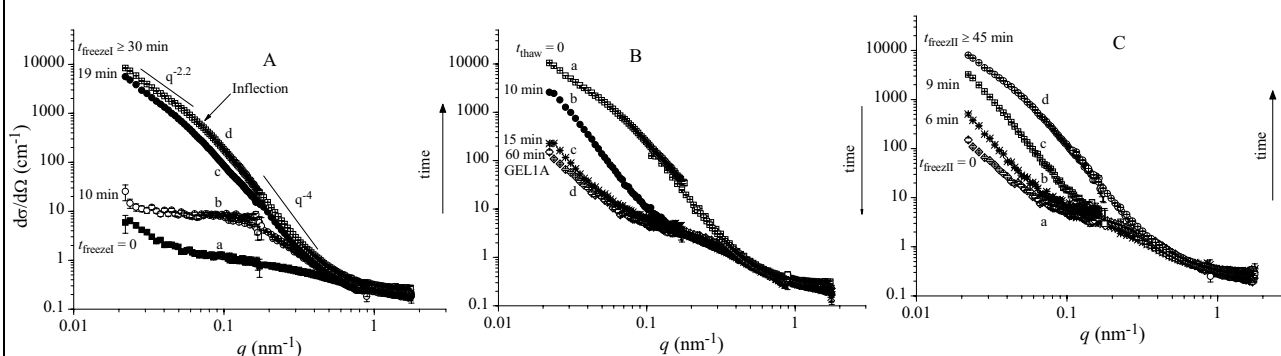


Figure 1. SANS curves from the solution with volume fraction of PVA equal to 0.086 during three consecutive steps made up of a first freezing at -13°C (A), thawing at 20°C (B), and II freezing at -13°C (C). The elapsed time (min) after each quenching is indicated.

During the freezing of the initially homogeneous solutions, the crystallization of the solvent is not complete, but an unfrozen liquid microphase having eutectic composition is also formed as indicated by curve d of Figure 1A that presents an inflection point at $q = 0.07 \text{ nm}^{-1}$ and two power law dependence in q in the two regions separated by the inflection point. This process is fast, and is accompanied by the confined crystallization of PVA inside the unfrozen microphase (Figure 2). Crystallization of PVA, in turn, is slowed down by vitrification.

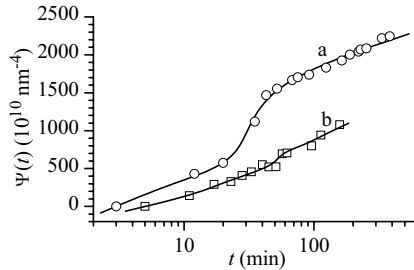


Figure 2. Crystallization of PVA in the unfrozen liquid microphase is indicated by increase of the scattering invariant ($\Psi(t)$) of PVA solutions at different concentrations evaluated from the SANS data collected in the q range $0.1 - 1 \text{ nm}^{-1}$. (a) Solution with volume fraction of PVA equal to 0.086; (b) Solution with volume fraction of PVA equal to 0.042.

Upon thawing (Figure 1B), ice crystals melt, obtaining a transparent gel that becomes opaque in ~ 200 min, due to a slow and progressive increase of the size of micro-heterogeneities (dilute and dense regions) imprinted during the fast freezing by the crystallization of water.

The present study shows conclusive evidences that the physical cross-links responsible for the formation of the microgel fraction acting as building blocks for the development of the macroscopic gel network in these systems are crystallites, that form already in the early 60 min of fast freezing. The crystallization of PVA in confined environment of eutectic composition is general, but the formation of a macroscopic gel occurs only for solutions with PVA concentration higher than a critical value, via the clustering association of the droplets of the microgel fraction. This is indicated by significant differences between the SANS curves from frozen solutions more concentrated in PVA (curves a and b of Figure 3) that form a gel upon thawing and that of a less concentrated PVA solution (curve c of Figure 3) that does not form a gel even for prolonged time at -13°C .

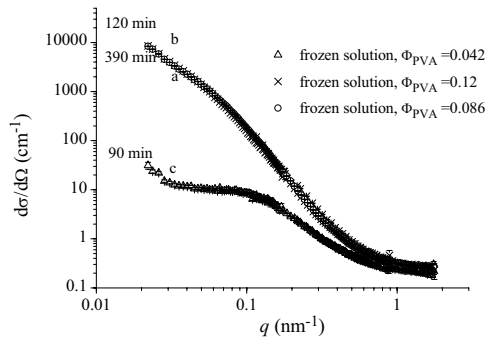


Figure 3. Comparison of the SANS curves recorded at -13°C from the frozen solution with volume fraction of PVA equal to 0.086 at the end of I freezing (curve a, 390 min freezing) with those from frozen solutions with volume fraction of PVA equal to 0.042 and 0.12 after ≈ 90 and ≈ 120 min freezing at this temperature, respectively (curve b and c, respectively) (B).

For solutions with PVA concentration below a critical value, indeed, the droplets of unfrozen liquid microphase remain isolated entities in the ice matrix (curve c of Figure 3).



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

Proposal number:	KW1-05-002		
Experiment title:	Interaction of phenol with PNIPA gels		
Dates of experiment:	23-25/05/2005	Date of report:	09/01/2006
Experimental team: Names	Addresses		
E. Geissler K. László	Laboratoire de Spectrométrie Physique, Université J. Fourier de Grenoble, 38402 St Martin d'Hères cedex, France Department of Physical Chemistry, Budapest University of Technology and Economics, H-1511 Budapest, Hungary		
Local Contact:	Vitali Pipich		

Experimental report text body

SANS measurements were performed on a series of PNIPA gels swollen either in pure D₂O or in the contrast matched condition 82%H₂O/18%D₂O, with varying amounts of deuterated phenol. Three sample-detector distances were used, and in the case of the contrast matched samples, counting times at the longest distance amounted to 6 hours to ensure reasonable statistics. Figure 1 shows the results for unfunctionalized PNIPA gels. The strong signal from the gel in D₂O consists of a power law behaviour at low q together with a scaling law of the form $a/(1+(q\xi)^2)^{d/2}$, where the value of the fractal dimension was $d \approx 1.6$, which is consistent with that predicted by scaling theory. If all the phenol molecules were attached to the polymer chains, then they would exhibit the same structure factor $S(q)$ as the gel in pure D₂O. On the basis of this $S(q)$ and armed with a knowledge of the relative contrast factors of PNIPA in D₂O and deuterated phenol in the contrast matched solvent, as well of their corresponding concentrations, an estimate could be made of the fraction of phenol molecules in the sample that are in contact with the polymer. For the sample containing 44 mM phenol, the result, $(5 \pm 1)\%$, is consistent with macroscopic measurements of the uptake of phenol in this system. For the sample containing 20 mM phenol, on the other hand, the observed fraction was $(0 \pm 1)\%$, i.e. zero within experimental error. The precision of these results is a considerable improvement on that of dynamic light scattering [1], which detected no adsorbed phenol in either case. An account of these measurements will appear in the NATO ASI series of a workshop in Kiev in November 2005 [2].

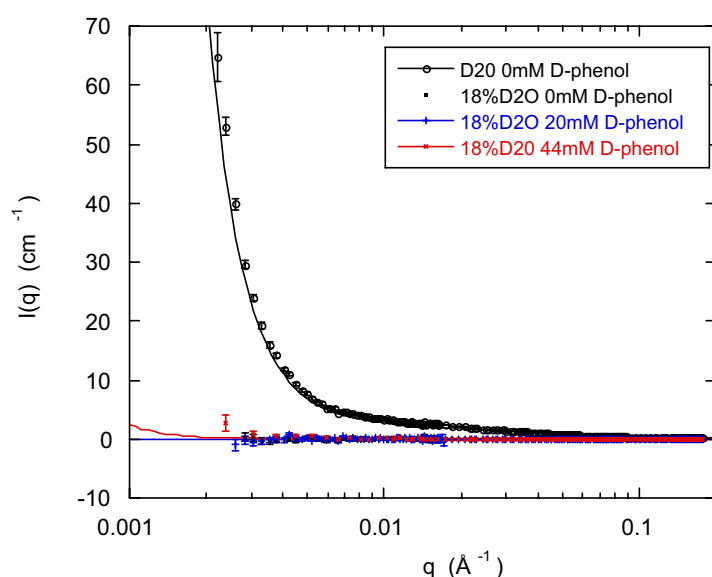


Figure 1. SANS curves from PNIPA in fully deuterated water and in contrast matches water at 18%D₂O. The continuous curves shown are proportional to the empirical fitting relation for the pure D₂O data,

$$I(q) = bq^{-3.2} + a \left[1 + (q\xi)^2 \right]^{0.8}$$

where $\xi=41$ Å, $b=2.7 \cdot 10^{-7}$, $a=3.4$ cm⁻¹.

Reference

- [1] K. László, K. Kosik, C. Rochas, E. Geissler *Macromolecules* **36**, 7771-7776 (2003).
- [2] K. László, K. Kosik, E. Wilk, E. Geissler: Interaction of Phenolic Pollutants with PNIPA Hydrogels, NATO ARW "Pure and Applied Surface Chemistry and Nanomaterials for Human, Life and Environmental Protection, NATO ASI Series, in press



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

Proposal number:	KW1-05-006		
Experiment title:	Determination of the stability range of a microemulsion		
Dates of experiment:	17.02.05	Date of report:	09.05.05
Experimental team: Names	Addresses		
Reiner Zorn Maria Mayorova Wim Pyckhout-Hintzen	IFF, FZ Jülich		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

The droplet microemulsion to be studied here has the peculiar property that the hydrophilic and hydrophobic components undergo glass transitions well separated in their dynamics. It is thus possible to study the glass transition dynamics of propyleneglycol (PG) confined to spheres of about 5 nm. These kind of investigations have been of increasing interest during the last years. For the materials here, dielectric experiments were already done [1] and experiments using inelastic neutron scattering at ILL Grenoble and FZ Jülich are planned.

Before starting the dynamical experiments it is necessary to check whether the microemulsion preserves its structure in the temperature range where those experiments are planned. SANS data on a similar system (D₂O/AOT/decane) [2] indicate that at about room temperature an aggregation of droplets takes place (Fig. 1). This would restrict the temperature range for the dynamic experiments in the worst case making the latter unfeasible.

We therefore performed SANS on a microemulsion which – apart from the fact that we use normal AOT instead of deuterated which is too precious for this test – is identical to that to be studied by inelastic neutron scattering. The temperature range chosen was that which is spanned by the inelastic experiments in the ‘worst case’, i.e. –20 ... +73.5°C.

The composition of the microemulsion used was h-PG: 10.2% / h-AOT: 36.1% / d-decahydronaphthalene (d-decalin): 53.7% (equivalent wt% of undeuterated compounds). To take care of the background, pure d-decalin was subtracted. Its scattering was about 1/30 of that of the microemulsion so that the resulting correction was only minor.

Fig. 1 shows SANS data from the lowest, highest, and one intermediate temperature exemplarily. It can be seen that except for a change in intensity the scattering due to thermal expansion does not change. If at all, a slight but continuous change of the droplet dimension takes place. In any case a drastic change of the scattering pattern due to aggregation (as observed in [2]) can be excluded. This means that microemulsions of this type can be used for studies of the dynamics over a wide temperature range.

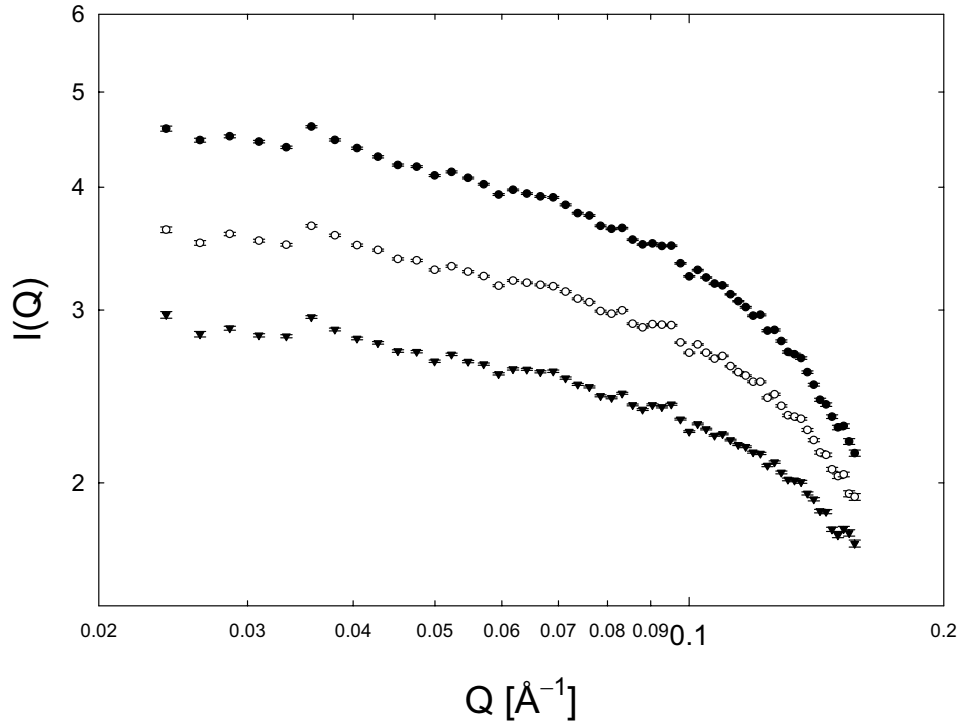


Fig.1: SANS patterns of the h-PG/h-AOT/d-decalin microemulsion for temperatures -20 ± 1 °C, $+17 \pm 1$ °C, and $+73.5 \pm 1$ °C

The secondary objective of the experiment, the determination of the droplet size, could not be fulfilled. The naïvely calculated radius of gyration, $0.9 \dots 1.0$ nm is far too small to be compatible with the estimate from the composition, 2.7 nm. The probable reason for this is that the microemulsion is rather concentrated. This means that the structure factor has to be taken into account: $I(Q) = P(Q)S(Q)$. Since $S(Q)$ increases at low Q this leads to a reduction of the slope of the Guinier plot, i.e. a reduction of the apparent R_g .

Because the calculation from composition shows that the droplet diameter is already close to the droplet distance (for the contrast here which includes the AOT shell in the “droplet”) we refrain from fitting this data with a model. Rather we will propose to repeat the experiment with a contrast showing the PG core selectively.

- [1] Lin-Min Wang, Fang He, R. Richert, *Phys. Rev. Lett.* **92**, 095701 (2004)
- [2] L. Arleth; J. S. Pedersen, *Phys. Rev. E.* **63**, 061406 (2001)



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

Proposal number:	KW1-05-007		
Experiment title:	Investigating the decomposition of MAO by contrast variation		
Dates of experiment:	15.06. – 16.06.2005	Date of report:	28.06.2006
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jörgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Coates et al. [1] reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. However, the kinetics and mechanism of living olefin polymerization is still poorly understood. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization.

Although MAO, $\text{Al}(\text{CH}_3)_3 \cdot \text{O}$, is a well established compound in olefin polymerization, nearly nothing is known about its structure. Only from pfg- ^1H -NMR experiments a dynamic radius of approximately 10-15 Å was estimated.

In a first experiment we investigated the aggregation behaviour of the h-MAO in d-toluene by SANS. We found two species of particles contributing to the scattering intensity. The first is the primary aggregate of MAO, which forms a Gaussian chain-like structure with an approximate size of ~ 50 Å. The second species has a characteristic size beyond the spatial resolution capability of SANS and is visible only as a power law decay, $\sim Q^{-4}$, in the low-Q regime. Since the low-Q scattering shows a profound time-dependence, it can probably be attributed to decomposition products of the relatively instable MAO, which mainly contain

intermediate species with an atomic composition of approximately $\text{Al}_2\text{O}_{2.5}\text{CH}_3$, which finally forms amorphous Aluminiumoxide, Al_2O_3 .

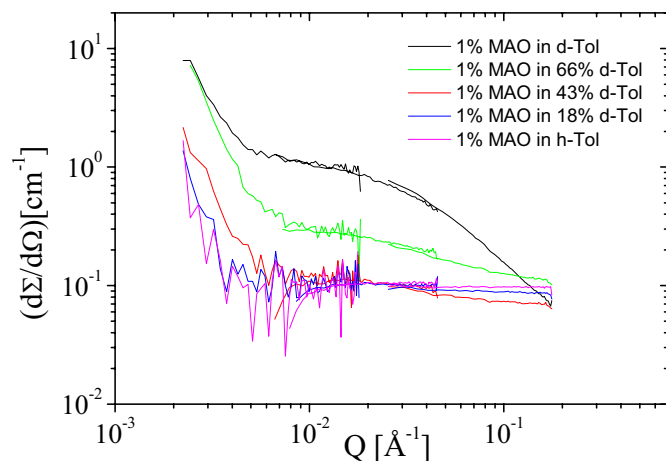


Figure 1 SANS profiles of contrasts variation of untreated 1% MAO solutions.

Now systematic investigations were performed: determine the composition of the decomposition products by contrast variation. Here 5 different were investigated for the untreated MAO, with scattering length densities adjusted to match either $\text{Al}_2\text{O}_{2.5}\text{CH}_3$, $\rho = 1.79 \times 10^{10} \text{ cm}^2 \approx 18 \text{ vol.-% d-toluene}$ and Al_2O_3 , $\rho = 4.09 \times 10^{10} \text{ cm}^2 \approx 66 \text{ vol.-% h-toluene}$, plus both full contrast and one intermediate contrast, see Fig. 1. The SANS results show that the main decomposition products are not Al_2O_3 . The further data analysis and experiments on element analysis are in progress.

[1] J. Tian, P. D. Hustad, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 5134.



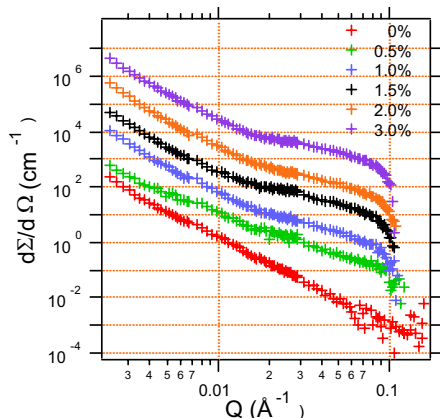
Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-05-008		
Experiment title:	Small Angle Neutron Scattering on Blends of Poly (Styrene-ran-Vinyl Phenol) with Liquid Crystalline Polyurethane		
Dates of experiment:	18.04. – 22.04.2005	Date of report:	22.06.2006
Experimental team: Names	Addresses		
Mark Dadmun Rujul Mehta	Chemistry Dept., University of Tennessee, Knoxville, TN 37996 Chemistry Dept., University of Tennessee, Knoxville, TN 37996		
Local Contact:	D. Schwahn		

Experimental report text body

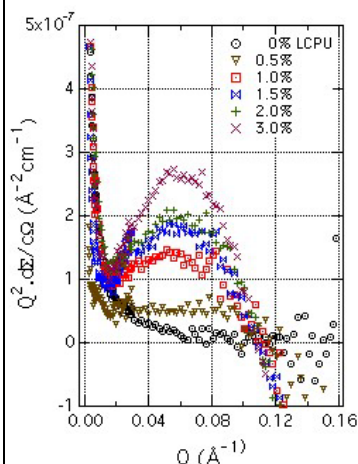
As result of our previous work [1], liquid crystalline polyurethanes (LCPU) are found to be miscible with a random copolymer of vinyl phenol (VPh) and styrene (dPS-VPh); with optimum hydrogen bonding between the -COOH groups of the LCPU and the -OH present in the styrenic matrix. Availability of a truly miscible molecular composite presents a unique opportunity of studying the conformation of polymer chains containing rigid-rods that are uniformly dispersed in a flexible coil matrix.

The LCPU (Mw 31700, PDI 1.64) and d8PS-VPh copolymer (12% VPh, M w 55700, PDI 1.42) were synthesized. Blends of LCPU and d8PS-VPh were prepared having compositions, 0.5-5%, (wt% LCPU). The SANS measurements were performed using the instrument KWS1 (Q range 0.02 to 1.6 nm⁻¹). Scattering curves of neat copolymer and the blends show a remarkable upturn in the scattering at low Q (Fig. 1). It is evident that VPh segments (not deuterated) in the random copolymer form a large-scale dynamically cross-linked structure, facilitated by the presence of hydrogen bonding within the VPh segments. Scattering curve for neat dPS-VPh fits reasonably well to the Debye-Bueche model in the low Q (<0.26 nm⁻¹). The correlation length of 27.3 nm obtained from this fit, represents the size of VPh aggregates that form the network.



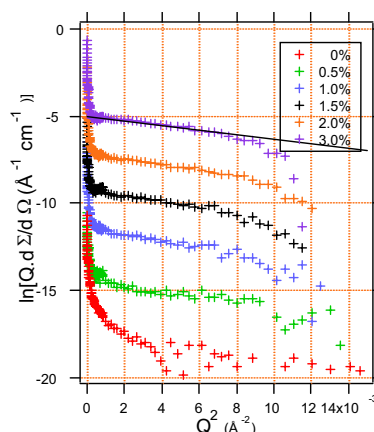
At higher Q ($>0.26 \text{ nm}^{-1}$), the scattering curve obeys the scattering equation given by Benoit et al [2], which describes cross-linked polymers with a characteristic negative intercept in the Zimm representation and yields the size of the vinyl phenol linkages, which form the network as 13.3 nm.

Addition of small amounts of LCPU in the scattering media resulted in a measurable change in the character of the scattering. A substantial reduction in the scattering is observed, within the low Q range (curve due to 0.5%); indicating that LCPU molecules act to disrupt the hydrogen bonded ensemble. Thus, we infer that the presence of a large scale structure in the copolymer is due to intra-species hydrogen bonding within the VPh segments of the copolymer; an arrangement that is measurably disrupted by addition of small amounts of LCPU, with a reduced correlation length of 22.5 nm.



What is interesting to observe in these curves is the additional scattering that occurs in the blends in the mid to high Q regime ($>0.16 \text{ nm}^{-1}$), which is clearly seen in the Kratky representation [3]. In the case of neat copolymer, scattering from copolymer chain segments that are forming the network result in a plateau approached from above. Interestingly, the scattering data from copolymer-LCP blends show a clear deviation from the plateau (Fig. 2). This additional scattering contains the information regarding the conformation of the LCP molecules.

The excess scattering not present in the data from the pure copolymer was fitted to the Kratky-Porod worm-like chain (KPWC) model. KPWC model describes scattering arising from a thin needle and is applied to systems containing rigid rods. Figure 3 shows the linear fit of the scattering data to the KPWC model providing a clear



- evidence of presence of rod-like structures within the blend. The cross-sectional radius of gyration obtained from this fit ranges from 26 nm to 15 nm, and serves as an indication of the cross-sectional size of the LCP rigid rods. The mid-high Q data was also fitted to a Zimm plot, providing a molecular weight of the rigid rods as 32985. This is in agreement with the M_w of the LCPU measured by GPC (31700). The length of the rigid rods obtained from KPWC fit ranged from 72.5 to 180.1 nm.
1. Macrom. Rapid Comm. 2001, 22, 779; Polymer 2000, 42, 1591; Macrom. 2002, 35, 5049; Macrom. 2003, 36, 3196
 2. Macrom. 1993, 26, 579
 3. Macrom. 1991, 24, 1269



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

Proposal number:	KW1-05-009		
Experiment title:	β-cyclodextrin in hydrophobically modified alginate solutions		
Dates of experiment:	31.08.2005 – 05.09.2005	Date of report:	15/02/2006
Experimental team: Names	Addresses		
Céline Galant Kenneth D. Knudsen	Department of Physics, Institute for Energy Technology, P. O. Box 40, N-2027 Kjeller, Norway		
Anna-Lena Kjørnisen Bo Nyström	Department of Chemistry, University of Oslo, P. O. Box 1033, Blindern, N-0315 Oslo, Norway		
Reidar Lund	IFF-Neutronenstreuung, Forschungszentrum Jülich, D-52425 Jülich, Germany		
Local Contact:	W. Pyckhout-Hintzen, D. Schwahn		

Experimental report text body

We proposed to study the properties of new supramolecular structures obtained by mixing in water a hydrophobically modified biopolymer (HM-alginate) and a branched polymer of beta-cyclodextrin (poly(β -CD)). It was expected that the formation of inclusion complexes between the hydrophobic segments of HM-alginate and the β -CD cavities of poly(β -CD) results in a system with i) thickening properties because of the aggregation between both polymers, and ii) specific inclusion properties related to the presence of β -CD units available for the complexation of additional molecules (i.e. hydrophobic drugs, for example). Combination of properties i) and ii) makes the HM-alginate/poly(β -CD) system a potential candidate for biomedical applications such as controlled drug delivery.

SANS spectra from HM-alginate (1.0 wt.)/poly(β -CD) mixtures in D₂O, have been collected with varying concentrations of poly(β -CD), at T = 25°C (Figure 1). Data collected for separated solutions of each of the polymers have also been collected and serve as reference in the process of evaluating the effect of mixing the two components.

Analysis of the SANS data shows that the clustering strength (1) of the mixtures rises with increasing poly(β -CD) concentration in the HM-alginate solution. The formation of aggregates with increasing size is characterized by an enhancement of the low q scattering as the poly(β -CD) concentration is increased. Because both components are protonated, it was not possible to use the contrast matching method. However, the scattering intensity of HM-alginate appeared very weak compared to that of poly(β -CD). Consequently, it has been assumed that the scattering from the poly(β -CD) in the mixtures is the dominating contribution to the total scattering intensity.

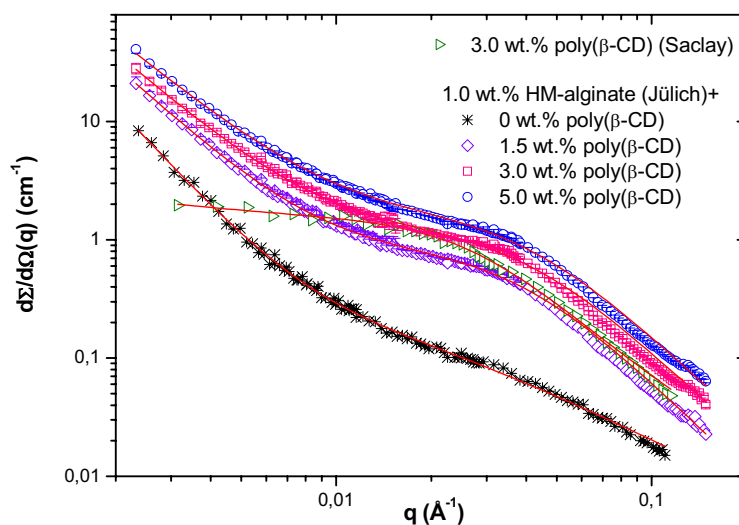


Figure 1. Influence of the poly(β -CD) concentration on SANS from HM-alginate (1.0 wt.%)/poly(β -CD) mixtures in D₂O, at T = 25°C. The green triangles ($\triangleright$) refer to the scattering from a poly(β -CD) solution (3.0 wt.%) in D₂O, measured at Saclay.

Based on the power law behavior of the scattering, a picture of the clusters structure has been proposed, where the HM-alginate chain interacts with the branched and compact architecture of poly(β -CD) only at the surface of the latter via inclusion complex formation between the HM-alginate hydrophobic segments and the β -CD cavities, thus making the inner structure of the poly(β -CD) unaffected (Figure 2).

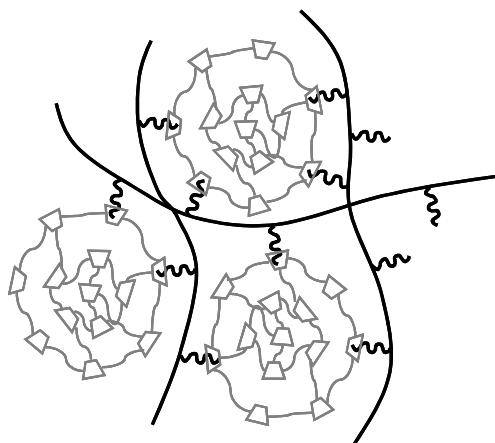


Figure 2. Scheme of the structure of a cluster resulting from inclusion interactions between the HM-alginate (represented in dark) and the poly(β -CD) chains (represented in grey).

(1) Hammouda, B.; Ho, D. L.; Kline, S. *Macromolecules* 2004, 37, 6932.



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

Proposal number:	KW1-05-011		
Experiment title:	Structural Investigation of inorganic salt nanoparticles confined in reversed micelles		
Dates of experiment:	10-12 June 2005	Date of report:	25.03.06
Experimental team: Names	Addresses		
Prof. M. Gradzielski	Technische Universität Berlin, Stranski-Laboratorium für Physikalische Chemie und Theoretische Chemie, Sekretariat TC 7, Strasse des 17. Juni 124, D-10623 Berlin (Germany)		
Dr. Cristina Giordano			
Local Contact:	Dr. W. Pyckhout-Hintzen		

Experimental report text body

The preparation and characterization of nanoparticles of inorganic salts is a highly active topic of current scientific research due to its large potential for applications [1, 2]. Among the various physical and chemical methods employed to obtain such nanoparticles, an interesting and promising route is based on the use of solutions of nearly dry reversed micelles as confining media since they easily allow both the entrapment and the stabilisation of very small nanoparticles of water-soluble salts within the hydrophilic core of reversed micelles or surfactant liquid crystals [3, 4]. The procedure allowing the preparation of such systems has been described in previous reports [5,6].

The formation of inorganic salts nanoparticles in the liquid samples was ascertained by SAXS [5, 6] and for the solid salt/surfactant composites, by WAXS and transmission electron microscopy (TEM). A typical TEM micrograph of a composite is shown in fig. 1. It can be noted that during the solvent evaporation an initial crystallization process takes place that leads to larger nanoparticles in the solid composites [5].

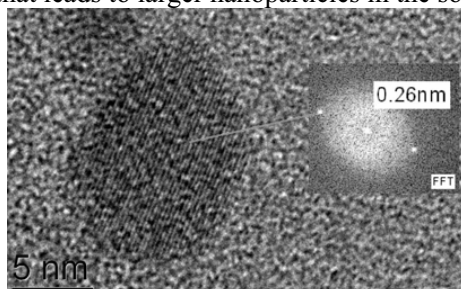


Fig. 1: TEM micrograph of a CoCl_2 nanoparticle in AOT matrix clearly showing the crystalline layering of $2.6 \text{ \AA}$.

However, for a more detailed structural picture, especially for very small nanoparticles of 1-4 nm size we performed these SANS measurements. The SANS technique, by means of external contrast variation, allows for a simultaneous determination of the size of the inorganic nanoparticles in liquid phase and their surrounding surfactant shell by choosing properly the contrast of the oil phase. In particular, we have investigated various inorganic salts (Cobalt (II) chloride and Yttrium (III), Copper (II), Barium (II) and Ytterbium nitrate) entrapped within the core of AOT reversed micelles dispersed both in D-Octane and H-Octane. Results showed that the entrapment of ionic clusters involves an increase of the micelle radius which is correlated with the salt/surfactant molar ratio (R_s). For each salt investigated, indeed, experiments were performed using two R_s values in order to study the effect of this parameter on the micellar size.

Figure 2 shows SANS scattering profiles of Yb(III) nanoparticles-containing in AOT reversed micelles dispersed in an organic solvent using a contrast variation, for an independent determination of the scattering from the core and from the shell

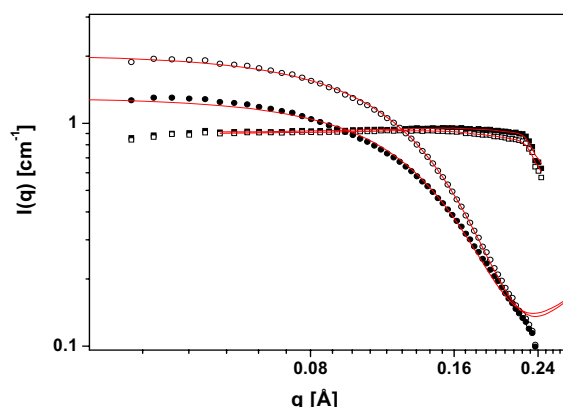


Fig 2: SANS curves of Yb(III) nanoparticles-containing in AOT reversed micelles, at two different salt/AOT molar ratio (R_s), dispersed in D-Octane (circles) and H-Octane (squares), respectively. Yb(III)/AOT/D-Octane at $R_s=0.04$ (●, R : 16.3 Å) and $R_s=0.085$ (○, R : 17.3 Å) and Yb(III)/AOT/H-Octane at $R_s=0.04$ (■, R : 4.7 Å) and $R_s=0.085$ (□, R : 5.7 Å). It can be noted that by increasing R_s an increase of the micellar core radius is observed.

Taking into account that the mean radius of bare AOT reversed micelles in D-hydrocarbon is around 15.0 Å [7], depending on W (the [water]/[surfactant] molar ratio), the present experimental data emphasize that salt is confined in form of very small nanoparticles (nanoparticle core radius around 5 Å). Results are in good agreement with SAXS results (R :10.8 Å, $R_s=0.05$ and R :11.1 Å, $R_s=0.11$), considering that SAXS is due to the contrast between regions with different electron densities and considering the reversed micelle structure, so that R must be interpreted as the mean radius of the hydrophilic micellar core (salt+head groups).

However, it was not yet possible to establish detailed and general relationship between R_s and R , and accordingly more detailed experiments still have to be done, in which the composition of the samples that is governed by R_s and also the type of salt contained have to be varied systematically, as also the type of salt employed appears to play a decisive role.

References

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- [2] P. Ball, L. Garwin, *Nature*, 355, 761 (1992)
- [3] J.H. Fendler, *Chem Rev* 87, 877 (1987)
- [4] V. Turco Liveri, In: Rosoff M (ed) Nano-surface chemistry, vol 1. Dekker, New York, pp 473-504 (2002)
- [5] C. Giordano, A. Longo, V. Turco Liveri, A.M. Venezia, *Coll. Polym. Sci.* 281, 229 (2003)
- [6] C. Giordano, A. Longo, A. Ruggirello, V. Turco Liveri, A.M. Venezia, *Coll. Polym. Sci.* 283, 265 (2004)
- [7] Gorski, Ostanevich, *J.I Phys.* IV 3, 149 (1993)



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

Proposal number:	KW1-05-012		
Experiment title:	<i>In vivo</i> characterisation of crowding in Escherichia coli cells		
Dates of experiment:	07/06/2005	Date of report:	8/12/2005
Experimental team:			
Names	Addresses		
Marion Jasnin	IBS 41 rue Jules Horowitz 38027 Grenoble Cedex 1 France		
Joseph Zaccai, Kathleen Wood	ILL 6 rue Jules Horowitz BP 156 38042 Grenoble Cedex 9 France		
Local Contact:	Martine Heinrich		

Experimental report text body

E. coli is a rod-shaped bacterium of $0.8\mu\text{m} \times 2\mu\text{m}$, surrounded by a membrane of about $300 \text{ \AA}$ thick. In a simple description, the cell is made up of three types of macromolecules: lipids, proteins and RNA, which represent 87% of the *E. coli* total dry weight. The cytoplasmic membrane consists in a lipid bilayer with membrane proteins (60% w/w). Inside the cell, RNA is mainly localised inside ribosomes, large macromolecular machines that contain both proteins (40%) and RNA (60%) and represent 25% of the macromolecular dry weight. The cell cytoplasm also contains cytoplasmic proteins. In the present work, we used small angle scattering and the solvent contrast variation technique on whole *E. coli*, to match successively lipids, proteins and RNA, and investigate the molecular crowding *in vivo*. Lipids are matched out at 11% D_2O , proteins at 41% D_2O and RNA at 68% D_2O . Membrane is also matched out at 20% D_2O and ribosomes at 56% D_2O .

Two types of sample were examined on KWS-1: high concentrated cell sample (*E. coli* paste) and diluted *E. coli* (10 mg/ml cell paste, dilution 1:20). For each of these two samples, cells were observed in buffer containing 0, 12, 22, 41, 54, 68, 80 and 100% D_2O . SANS experiments were performed with a wavelength of $7 \text{ \AA}$ at KWS-1. Three sample-to-detector distances (2, 8 and 20 m) were employed to cover a Q-range of $0.002\text{--}0.2 \text{ \AA}^{-1}$. 2-D data were corrected pixel wise for instrumental background and detector efficiency, and radial averaged over the full detector. In parallel, two solvent conditions (0 and 100% D_2O) for paste samples were examined on KWS-3, to acquire a wide range of scattering vector for extreme solvent conditions (from 10^{-4} to $10^{-3} \text{ \AA}^{-1}$ on KWS-3 and from 10^{-3} to $10^{-1} \text{ \AA}^{-1}$ on KWS-1).

The experiments revealed an anisotropic distribution of the intensity for the paste samples, which became isotropic after dilution. Another important feature, already observed during the precedent experiment, is the presence of a main peak around Q equals $0.02 \text{ \AA}^{-1}$ for both types of sample. We reported in Fig 1.a the Q-dependence of the scattering cross-sections for the paste samples, radial averaged over the full detector that gives an acceptable approximation for the anisotropic spectra. The anisotropy for the intensity results in a shifting in Q of the peak position, depending on the sample. Since the anisotropy disappears after dilution, we attributed the anisotropy to the cell paste preparation, in particular to the ordered stacking of the bacteria during centrifugation.

The peak reveals the presence of a structure which repeats itself inside the sample. We previously thought about the periodical stacking of planar objects, separated by about 330 Å, as given by the Q-value of the peak. (The real position of the peak is given by the diluted curves. Only the scattering intensity of the 100% D₂O diluted sample was sufficiently high to reveal a clear peak, at Q equals 0.019 Å⁻¹ (Fig.1.b)).

This hypothesis was checked by the contrast variation technique. The contribution of the different component inside the cell was extracted, using their various compensation points. We looked at the influence of the contrast on the peak intensity (without taking into account the precise position of the peak). Fig. 2 represents the intensities at each contrast and Fig. 3 the corresponding Guinier plots, both between Q equals 0.01 and 0.05 Å⁻¹ that corresponds to the Q-range of macromolecules. It reveals a very large peak at high contrasts: 68% D₂O (match point of the RNA), 80% and 100% D₂O. At 41% D₂O, compensation point of the proteins, the peak becomes smaller and it disappears at 22% D₂O (match point of the membrane) and 12% D₂O (match point of the lipids). At 0% D₂O, a small peak appears. All the scattering curves confirm that the peak arises from the membrane. Membrane is made up of lipids (40% w/w) and proteins. Obviously, the peak is matched out when membrane and lipids are matched out. At 41%, the peak is not as intense as at high contrasts (such as 68%) where the contribution due to the lipids and proteins dominates, which is in good agreement with the matching of membrane proteins.

Moreover, a radius of gyration was extracted from the Guinier plot at 22% D₂O and found to be 65 Å, which corresponds to the radius of gyration of the ribosome, only visible when the membrane is matched out.

Moreover, it becomes clear that the anisotropy distribution for the paste sample intensity must be due to the ordered stacking of the membrane during centrifugation.

This experiment is of fundamental importance because it put into light that it is possible to isolate the contribution of different part of the cell under molecular crowding conditions. Non dynamical mapping of the cell is possible *in vivo*, using the contrast variation technique. It opens the way to new amazing experiments that could enrich in a very unique way the knowledge about whole cell.

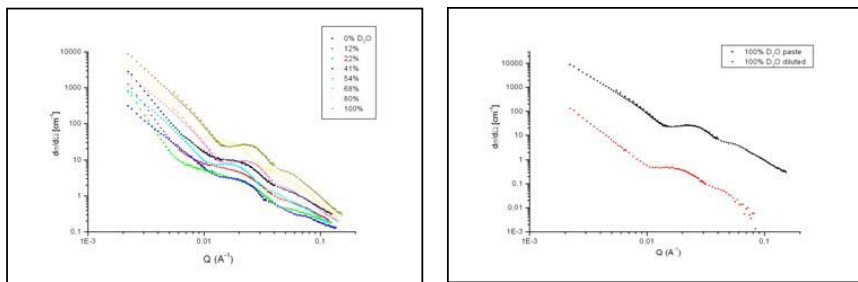


Fig1.a Q-dependence of the scattering cross-sections for the paste samples, radial averaged over the full detector. 1b. 100% D₂O paste and diluted samples.

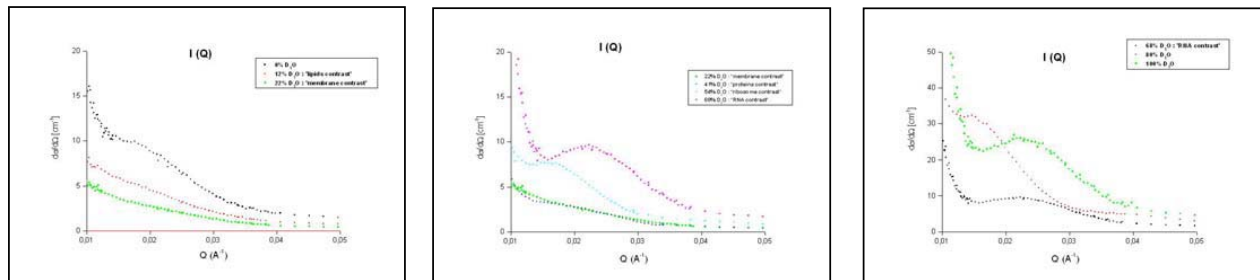


Fig2. Q-dependence of the scattering cross-sections for the paste samples (linear scale)

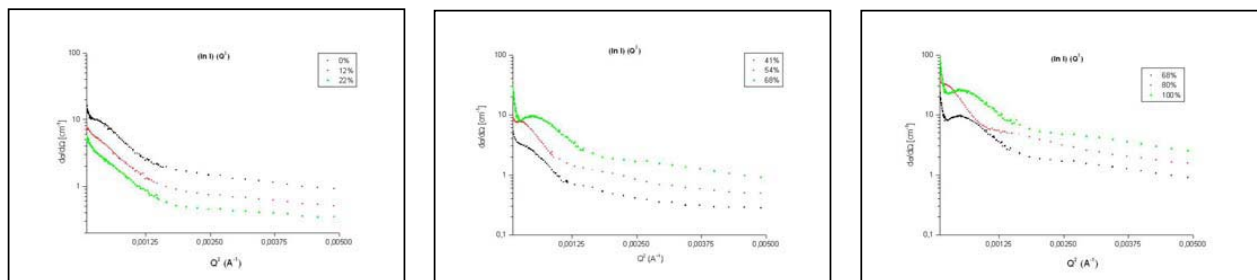


Fig3. Guinier plots for the paste samples.



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

Proposal number:	KW1-05-014		
Experiment title:	Micellar properties of PB-PS-PB triblock copolymers in alkanes: Kinetics of chain exchange.		
Dates of experiment:	22.04. – 25.04.2005	Date of report:	14.6.2006
Experimental team: Names	Addresses		
Reidar Lund Lutz Willner Hermis Iatrou	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich University of Athens		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

Recently, we have studied the equilibrium chain exchange kinetics in diblock copolymer micelles by time resolved small angle neutron scattering (TR-SANS). The principles of this novel technique have already been published /1/. Three structurally different systems have been investigated: i) a starlike micelle prepared from an asymmetric poly(ethylene-*alt*-propylene) – poly(ethylene oxide) (PEP-PEO) diblock copolymer in water/dimethylform - amide (DMF) as selective solvent mixture for PEO, ii) a compact micelle obtained from a symmetric polystyrene-polybutadiene (PS-PB) diblock in DMF as selective solvent for PS, and iii) the inverted analogue formed by the same PS-PB diblock in n-alkanes ($C_{10} - C_{16}$) which are all selective for PB. The latter micelles contain 35 - 50% solvent in the core. The observed exchange kinetics in each of these micellar structures reveals as a general characteristic behaviour a very broad distribution of relaxation rates which in fact follows a logarithmic time decay. This clearly deviates from a single exponential predicted by the theory of Halperin and Alexander /2/. This theory describes the exchange by a simple insertion/expulsion mechanism of single unimers based on the classical Aniansson and Wall mechanism derived for low molecular surfactant micelles.

The observed logarithmic time dependence can neither be explained by the polydispersity of the block copolymers and/or by different micellar sizes nor by parallel existing exchange scenarios like fusion and fission or isotope effects. Instead the observed time dependence is associated with “hierarchical constrained dynamics”, i.e. dynamics which involves a sequence of correlated processes characterized with an increasing characteristic time. We have attributed these processes to strong coupling of the chain dynamics induced by the confinement and topological interactions in the core /3,4/.

In the present study we have investigated the effect of polymer chain architecture on the exchange kinetics. A change in polymer architecture drastically changes the topological situation inside the micellar core. Therefore this experiment will elucidate the role of chain topology and core dynamics on the expulsion kinetics in

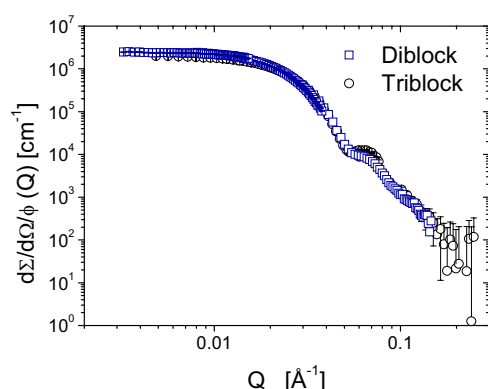


Figure 1 Core contrast measurements of d-PB10-h-PS10 diblock and d-PB10-h-PS20-d-PB10 triblock copolymers in hexadecane revealing identical PS-core size.

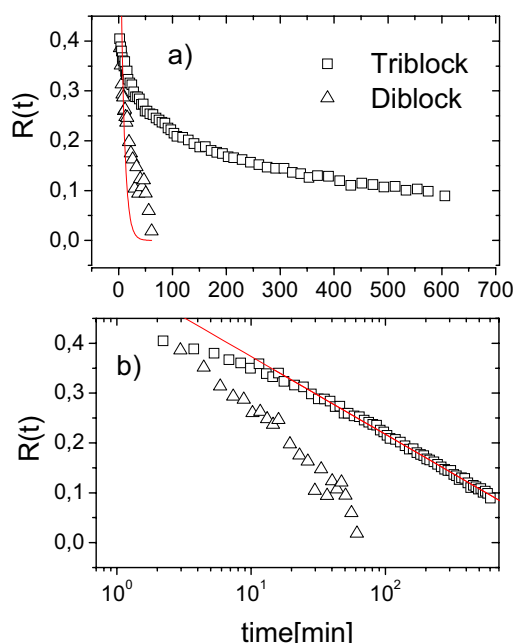


Figure 2a) Relaxation curves of the PS-PB diblock and triblock copolymers in dodecane. Solid line indicates a single exponential predicted by theory. b) lin-log representation of the same data. Solid line reflects the log time dependence.

with more dense cores. We explain this by increased chain correlations in the core due to “knots” present in the triblock copolymer system. This directly confirms the importance of chain topological interactions on the exchange kinetics in polymeric micelles. We plan to model this in more detail in the future.

- /1/ Willner, L.; Poppe, A.; Allgaier, J.; Monkenbusch, M.; Richter, D. *Europhys. Lett.* 55 (2001), 667.
- /2/ Halperin, A.; Alexander, S. *Macromolecules* 22 (1989), 2403.
- /3/ Lund, R.; Willner, L.; Stellbrink, J.; Richter, D. *Phys. Rev. Lett* 96, 068302 (2006).
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polymeric micelles. As a model system we have chosen PB-PS-PB triblock copolymer micelles in n-alkanes as selective solvents. An ideal comparison is possible in case both polymers form micelles with the same core size. This can be expected from double diblocks: $(\text{PB10-PS10})_2 = \text{PB10-PS20-PB10}$.

Three triblock copolymers have been prepared for the present study: h-PB10-h-PS20-h-PB10, d-PB10-d-PS20-d-PB10 and d-PB10-h-PS20-d-PB10 with almost identical polymer characteristics. The partly labelled triblock copolymer, d-PB10-h-PS20-d-PB10, has been used to determine the structural details of the micelles by SANS/contrast variation experiments. An example is shown in Figure 1 which shows the core contrast measurements of the d-PB10-h-PS20-d-PB10 in comparison with the diblock analogue in hexadecane. These results show that the micelles have exactly the same structural characteristics since both curves lie on top of each other. In particular the amount of solvent in the core is seen to be identical. Thus the kinetics of the two micelles can be directly compared and a direct study of the influence of chain architecture can be made.

The two fully labeled triblock copolymers have been used for the TR-SANS study. Figure 2a) shows the corresponding relaxation curve in comparison with the one of the diblock. We have chosen a situation where the micelles contain a large amount of solvent, approximately 45%, therefore geometrical correlations in the core should disappear. This is observed for the diblock copolymer which gives a Halperin-Alexander like single exponential indicating that no chain correlations are present.

On the other hand compared to the diblock the kinetics of the triblock is drastically slower and again approaches the log time dependence for longer times as shown in Fig. 2b. Hence the topological constraints in the triblock are significantly affecting the kinetics and gives rise to a similar coupling between the chains as observed for the diblocks



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

Proposal number:	KW1-05-017		
Experiment title:	Nanoparticles of calcium phosphate, functionalised with DNA		
Dates of experiment:	14.04.2006	Date of report:	17.05.2006
Experimental team: Names	Addresses		
Viktoriya Sokolova Oleg Prymak Matthias Epple	Institut für Anorganische Chemie Universität Duisburg-Essen Universitätsstraße 5-7 D-45117 Essen, Germany		
Vitaliy Pipich Dietmar Schwahn	Institut für Festkörperforschung Forschungszentrum Jülich D-52425 Jülich / Germany		
Local Contact:	Vitaliy Pipich		

Experimental report text body

In principle, a shell structure of a DNA/mineral complex can be proven with SANS by using the contrast matching technique. However, this technique only works when mineral and DNA have different scattering length densities. The scattering length density of crystalline calcium phosphate can be calculated ($\rho = 4.4 \times 10^{10} \text{ cm}^{-2}$), whereas ρ for DNA has to be determined experimentally. So, we first carried out measurements on five 7.5mg/ml DNA aqueous solutions of varying light and heavy water content; the scattering profiles are shown in Figure 1. In Figure 2 the square root of the scattering intensities at the peak maximum are plotted as function of the D_2O content. The intersection of the red and black (dashed) lines give the matching

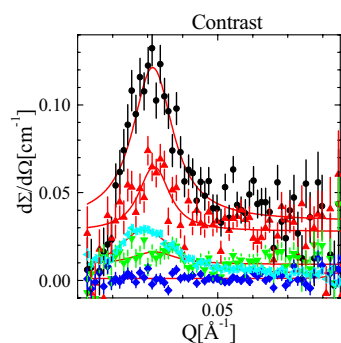


Figure 1. Scattering profiles from DNA in $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures

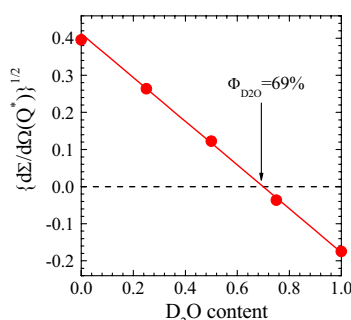


Figure 2. Scattering Contrast: DNA

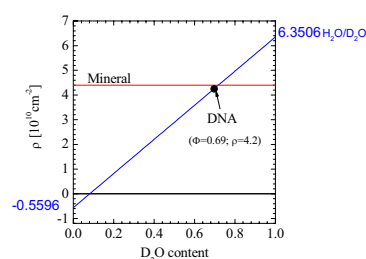


Figure 3. Matching points of DNA and calcium phosphate in $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixture

concentration of D₂O, namely $\Phi_{D_2O}=0.69$ giving $\rho=4.23 \times 10^{10} \text{ cm}^{-2}$. In Figure 3 the black circle corresponds to the matched scattering length density of DNA in H₂O/D₂O. The matching point of the mineral is defined by the intersection of the blue and red lines. We concluded from these measurements that the scattering length density of both components is very similar which does not allow a distinction of both components. Therefore we investigated DNA/mineral complex only in D₂O solution.

The DNA/mineral complexes were prepared as follow: (1C) 0.5ml of freshly mineralised calcium phosphate (0.0X M) was mixed with 0.5ml of 1mg/ml heavy water solution of DNA, stabilizing mineral growth by localization at the surface; (2C) two-shell particles were expected by addition of 0.5ml freshly mineralised calcium phosphate to 1ml of 1C-solution; (3C) 2C + 0.5ml of DNA mixture; (4C) 3C + 0.5ml of calcium phosphate mixture.

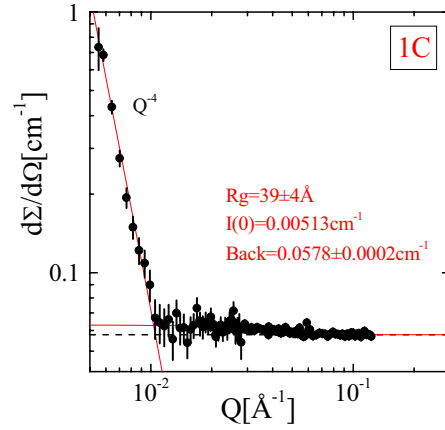


Fig. 4 Scattering curve for 1C-sample

In Figure 4 a representative scattering curve is depicted. As the mineral/DNA complex are larger than 2000 Å only the Q^{-4} tail of the form-factor is detected within the available Q -range. Scattering of unbound DNA can be easily separated in the Q -range above 10^{-2} Å^{-1} . So, the scattering signal $d\Sigma/d\Omega(Q)$ was fitted assuming an incoherent superposition of the signals from the mineral/DNA complex, unbound DNA and background according to

$$d\Sigma/d\Omega(Q) = P_4/Q^4 + I(0) \exp(-R_g^2 Q^2/3) + I_{BACK} \quad (1)$$

The amplitude P_4 is proportional to the total surface of the mineral/DNA complex; $I(0)$ the prefactor of the Guinier law and proportional to the concentration of unbound DNA; R_g the radius of gyration of unbound DNA; I_{BACK} the background scattering of D₂O.

Assuming a constant number of the mineral/DNA particles, the normalized scaling amplitude P_4 should continuously increase for the 1C to 4C samples. But from the experiment a continuous decrease is obtained (Figure 5). This means aggregation of the DNA/mineral complexes.

In Figure 6 the “step” dependence of the radius gyration of unbound chains calculated from high- Q range; the average value is $R_g=34 \text{ Å}$. In Figure 7 the “step” dependence of the forward scattering normalized to the volume of added DNA-mixture shows a dramatically decrease of the relative unbound chain number after the second step.

In conclusion, the growth of shells following the step-by-step addition DNA and mineral appears not the right model for the present samples. The DNA/mineral complexes showed a strong tendency of aggregation.

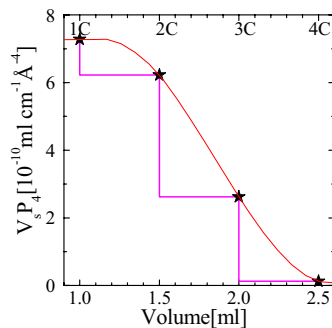


Figure 5 Surface of particles

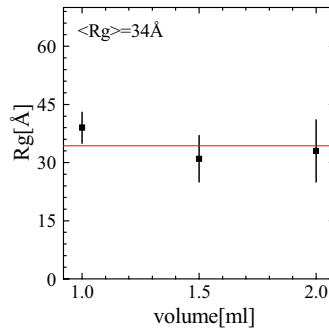


Fig. 6 Scattering from unbound DNA: R_g

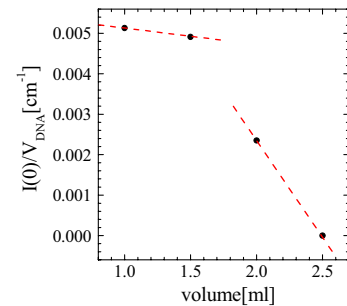


Fig.7. Scattering from unbound DNA: $I(0)$



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

Proposal number:	KW1-05-018		
Experiment title:	Scattering length density of h-PEO and d/h-PEO in H ₂ O/D ₂ O mixtures		
Dates of experiment:	21.-23. Feb. 2005	Date of report:	31. May 2006
Experimental team: Names	Addresses		
G. Rother ¹ J. Stellbrink D. Richter	Institut fuer Neutronenstreuung, Institut fuer Festkoerperforschung, Forschungszentrum Juelich, D-52425 Juelich		
Local Contact:	D. Schwahn		

Experimental report text body

The experiment aimed to study the scattering length density of poly- ethylene oxide in different mixtures of H₂O and D₂O. This experiment was stimulated by unexplained results for the small angle neutron scattering from PEP-PEO micelles. During the analysis it turned out that the description of the scattering data is not possible by using the nominal values of the scattering length densities of PEP and PEO. One possible explanation for this discrepancy is the preferential adsorption of one species from H₂O/D₂O mixtures to the PEO, which would virtually change the scattering length density of PEO. For that reason we preformed a contrast-variation experiment with h-PEO homopolymer dissolved in different mixtures of H₂O and D₂O. The data indicate some isotope effect. The results are still being examined.



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

Proposal number:	KW1-05-019		
Experiment title:	Form factor of silica aggregates in reinforced latex films		
Dates of experiment:	14.05. – 16.05.2005	Date of report:	23. 05. 2006
Experimental team: Names	Addresses		
Wim Pyckhout-Hintzen	Institut für Festkörperforschung, Forschungszentrum Jülich GmbH LCVN, Université Montpellier II, 34095 Montpellier Cedex, France		
Julian Oberdisse			
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

ABSTRACT:

Elastomers filled with hard and small particles are of great importance to the rubber industry. A former SANS study of our model systems, colloidal silica in PMMA/PBuA latexes, has dealt with the structure determination at fairly high volume fractions of filler. Therefore, modelling was somewhat hampered by the unknown shape of aggregates in the samples. This proposal aims primarily at the form factor of dilute silica aggregates in latex films to allow the higher concentration samples to be analyzed completely. We also planned to do a preparatory experiment, where we wanted to look at the deformation of the aggregates under uniaxial strain ($\lambda = L/L_0 = 1.5, 2., 2.5, 3. \dots$), but this could not be done due to lack of time and problems with the sample stretching.

CONTEXT:

In the past, we have investigated the structure and the rheological properties of silica aggregates embedded in a polymeric matrix made by coalescence and fusion of latex nanoparticles. Concerning the silica structure, the main findings are [1-4]:

- (i) A strongly pH (between 4 and 10, before solvent evaporation) and weakly silica concentration (between 3% and 15%v) dependent aggregation, higher pH yielding smaller aggregates (N_{agg} between a few beads and several thousand).
- (ii) A strong interaction peak between aggregates making the disentanglement of inter-aggregate structure and aggregate shape difficult.

The **aim of the present proposal** was to measure a first set of new samples at much lower silica concentration (between 0.5 and 2.5%v).

PRELIMINARY RESULTS:

In Figure 1a, the scattered intensity of a series of samples (fixed solution pH 7.5, varying silica volume fraction Φ in final nanocomposite) is shown in a $I(q)/\Phi$ presentation. The data overlaps nicely in the intermediate and large- q range. The overlap at high q means of course that the primary particle is the same. In the intermediate q -range, the overlap corresponds to an identical intra-aggregate organization. In this specific case, a power law $I(q) \propto q^{-2.7}$ reproduces the intermediate scattering quite nicely (this is also shown in Figure 1b). At small angles, a systematic deviation is observed: higher concentrations give lower reduced intensity. This means that the average aggregation number is lower at higher concentrations.

A similar evolution is observed at pH 7, where three more samples were measured at approximately identical silica volume fractions. In Figure 1b, we compare one of these intensities to the scattering of the individual bead, the form factor of which was measured at low concentration in heavy water. The high- q scattering was adjusted manually. The difference in small angle scattering gives the average aggregation number of the aggregates, approximately 100 in this case. The results for all samples are given in the tables below. It is found as expected that the aggregation number is higher at lower pH. More surprisingly, it depends rather strongly on the volume fraction. Additional experiments will be needed to see if this behaviour is reproducible.

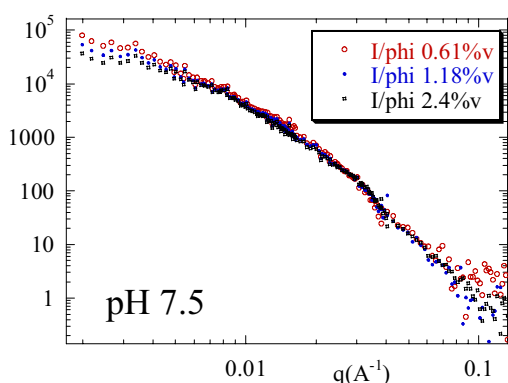


Figure 1a

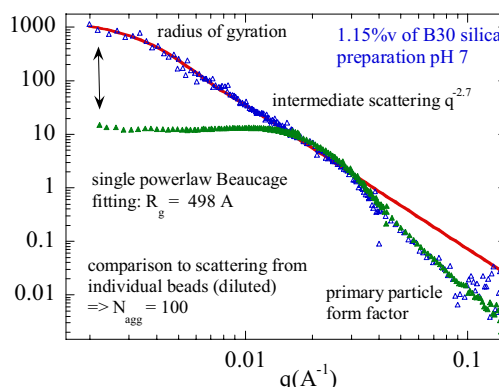


Figure 1b

A simple analysis of the data can be done in terms of a simple fractal law relating aggregate size and aggregation number: $N_{agg} = (R/a)^d$. Here R is the measured radius of gyration, a the primary particle radius, and d the fractal dimension ($d = 2.7$). The results are compared to the data in the tables below, assuming $a = 92$ Å. This number was chosen as an illustration because it reproduced nicely the behaviour for pH 7.5. In any event, it is of the right order of magnitude, the R_g of particles being approximately 100 Å. More elaborate analyses using Reverse Monte Carlo methods are currently undertaken.

Φ (pH 7.5)	R_g (Å)	I_0 (cm ⁻¹)	N_{agg}	$N_{agg}(\text{mod.})$
0.61%	485	588	90	90
1.18%	420	701	60	60
2.4%	348	930	36	36

Φ (pH 7)	R_g (Å)	I_0 (cm ⁻¹)	N_{agg}	$N_{agg}(\text{mod.})$
0.58%	564	1166	180	134
1.15%	498	1434	100	95
2.3%	458	2353	91	76

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

Proposal number:	KW1-05-020		
Experiment title:	Characterization of polyhexadiene polymers from living olefin polymerization		
Dates of experiment:	2005-05-16,17,18	Date of report:	2006-05-31
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jörgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Juelich Institut für Festkörperforschung, Forschungszentrum Juelich Institut für Festkörperforschung, Forschungszentrum Juelich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Polymeric materials are currently more indispensable to modern society than at any other point in history. Polyolefins are by far the most important commercial class of synthetic polymers. Several ground-breaking reports have appeared in the recent literature concerning living olefin polymerization. The importance of these living olefin polymerization catalysts is largely proportional to their ability to form block copolymers with high glass or melting transition blocks from common commercial monomers such as ethylene and propylene, as these materials have applications as compatibilizers and elastomers. In the last 5 years, there was a renaissance in living olefin polymerization, building rapidly on the foundation set solidly by Doi and coworkers over two decades ago. However, the kinetics and mechanism of living olefin polymerization is still poorly understood and there is no any scattering work has been done on this field. Coates et al. reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization.

In order to study the real living olefin polymerisation system efficiently, the investigations of activator-MAO, catalyst, mixture of MAO/catalyst and polymers solutions should be done in advance to get significant knowledge on the living olefin polymerisation system. Nice beam-time supports were offered for the MAO, Catalyst and mixture of MAO/catalyst characterization from KWS1 and KWS2.

Now a set of 4 polyhexadiene polymers with M_w of 10K-100K were prepared by Coates' group in Cornell University. The characterization of these polymers has been done in 4 concentrations for each polymer.



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

Proposal number:	KW1-05-021, KW1-05-043, KW1-05-038		
Experiment title:	Biom mineralization in the presence of the protein Ovalbumin: Freezing stop technique - contrast variation.		
Dates of experiment:	13.05. – 14.05.2006 04.10. – 07.10.2006 22.08. – 24.08.2006	Date of report:	31.05.2006
Experimental team: Names	Addresses		
V. Pipich D. Schwahn	Institut für Festkörperforschung Forschungszentrum Jülich D-52425 Jülich Germany		
Local Contact:	V. Pipich		

Experimental report text body

Controlled formation of nanostructures with predicted properties is a global aim of biom mineralization. The initial stage of mineralization is a crucial period in the formation of minerals as to large extend it determines the morphology of the final nanoparticles. Therefore, monitoring the early stages is an important topic. Small angle neutron scattering technique is a powerful tool for in vitro controlling the size and morphology of the growth of particles in the mineralization process. However, it is a rather slow technique as the accumulation time usually needs minutes whereas the crucial time of the initial time of mineralization are usually seconds or even less.

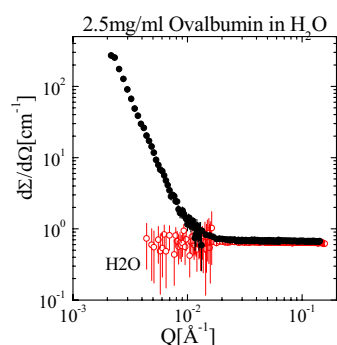


Fig.1. Scattering curves: ice and protein/ice complex

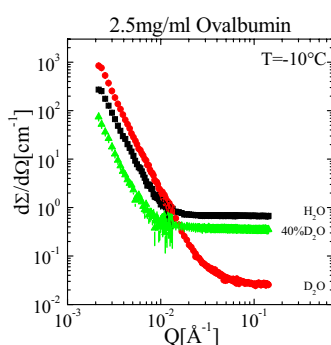


Fig.2. Scattering curves of protein/ice complex in: H₂O, D₂O and 40% D₂O.

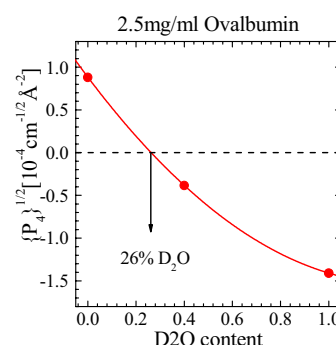


Fig.3. $\{P_4\}^{1/2}$ versus D₂O content.

Therefore, we tried to slow down the process of mineralization in two ways: (a) by freezing the sample in liquid nitrogen at the different stages; (b) by increase the viscosity of the solvent.

In Figure 1 the scattering profiles after quenching pure water (red circles) and 2.5 mg/ml protein Ovalbumin in water (black circles) in liquid nitrogen were measured at -10°C . The scattering signal from pure water contains only constant background, whereas the protein solution contains a signal from individual chains at high Q -range and scattering from aggregated proteins within the low Q -range. In order to check the reason for low Q -range scattering we carried out additional measurements with the proteins in D_2O and $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures. In Figure 2 the scattering curves of 2.5mg/ml protein Ovalbumin in H_2O , D_2O and 40% $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixture are collected. Even though the 40% D_2O content represents the matching condition for proteins the strong scattering signal is still present. The scattering signal follows Q^{-4} power law with the amplitude P_4 . In Figure 3 the square root of P_4 as function of D_2O content shows the matching point of the aggregate at 26%. Aggregation of proteins at freezing in liquid nitrogen induces inhomogeneous crystallization of water or formation of amorphous ice within the protein aggregates. Therefore, it is difficult to follow the mineralization process by freezing technique.

The second method of slowing down mineralization is the increase of the solvent viscosity. A glycerol/water mixture was selected as the biomineralization media. The crystallization temperature of pure glycerol(G) and water(W) is 20°C and 0°C , respectively, but their mixture with 67% glycerol content has a freezing temperature of -60°C . Therefore, by the variation of glycerol content we can vary the viscosity of the media over a broad range. Another advantage of this mixture is its widespread use as an agent for keeping of biomaterials in refrigerator.

In a first step we measured the conformation of the protein Ovalbumin in G/W mixture with 67% glycerol content. The scattering profiles of several concentrations of the proteins are presented in Fig.4(a). The simultaneous fit of SANS data by is Guinier law is shown by red lines. The radius of gyration is obtained $R_g=30\pm0.5\text{\AA}$. The forward scattering as function of the protein content shows linear dependence as demonstrated in Fig.4(b).

The mineralization reaction was carried out in G/W mixture with 67% glycerol content and neutral $\text{pH}=7$. Solutions of 0.1M calcium chloride and sodium carbonated were mixed directly in the Helma-cell, and then the scattering signal was measured at 20m sample-to-detector position every 10 minutes, during 12 hours. In Figure 5(a) the typical scattering curve from samples with and without protein. Within the measured Q -range the scattering curves follow a power law with the fractal exponent of 2.6 in both cases. Such kind of fractal dimension is characteristic for diffusion-limited aggregation.

The time evolution of the amplitude of the power law $Q^{-2.6}$ of the scattering curves with and without proteins is plotted in Figure 5(b). The shape of the time dependences of $P_{2.6}$ looks similar, but in the presence of proteins the scattering intensity is approximately 10% higher.

In conclusion, two methods of slowing down the mineralization process were tested by SANS. In the G/W mixture the aggregation of calcium carbonate particles occurred in a fractal structure. The size of the initially nucleated particles was limited by the high viscosity ($R<200\text{\AA}$), which afterwards formed fractal-like aggregates.

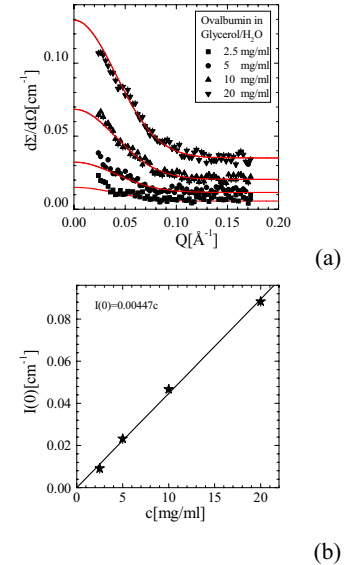


Fig.4. (a) Scattering curves: 2.5, 5, 10 and 20 mg/ml Ovalbumin in 67% glycerol mixture; (b) forward intensity of corresponding scattering curves.

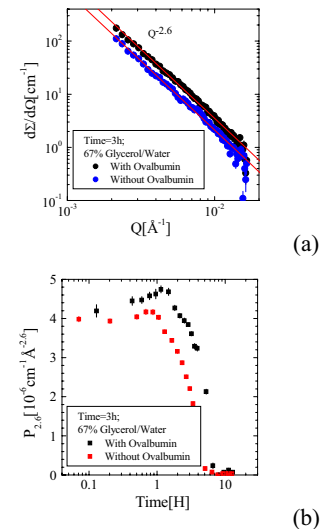


Fig.5. (a) Scattering profiles of mineral particles in 67% glycerol mixture with and without Ovalbumin; (b) scaling amplitude versus time



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

Proposal number:	KW1-05-022		
Experiment title:	Characterisation of a glass-forming microemulsion		
Dates of experiment:	20.06.05	Date of report:	30.09.05
Experimental team: Names	Addresses		
Reiner Zorn Maria Mayorova Wim Pyckhout-Hintzen	IFF, FZ Jülich		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

The droplet microemulsion to be studied here has the peculiar property that the hydrophilic and hydrophobic components undergo glass transitions well separated in their dynamics. It is thus possible to study the glass transition dynamics of propyleneglycol (PG) confined to spheres of nanometer size. These kind of investigations have been of increasing interest during the last years. For the material here, a propyleneglycol/AOT/decaline microemulsion, dielectric experiments were already done [1] and experiments using inelastic neutron scattering at ILL Grenoble and FZ Jülich are planned.

Before starting the dynamical experiments we wanted to determine the droplet size by SANS. An earlier SANS experiment (KW1-05-006) with h-PG/h-AOT/d-decaline isotopic composition showed that no aggregation of droplets takes place. The size of the droplets could not be determined unambiguously but the results already indicated that the droplet size would be much smaller than expected, about 1 nm.

Therefore, we now performed SANS on a microemulsion with hdd isotopic composition. We used detector distances of 1.25 m and 2 m yielding a Q range from $0.023 \text{ \AA}^{-1}$ to $0.25 \text{ \AA}^{-1}$.

The composition of the microemulsion used was h-PG: 10.2% / d-AOT: 36.1% / d-decahydronaphthalene (d-decalin): 53.7% (equivalent wt% of undeuterated compounds). To take care of the background, pure d-decalin was subtracted. Its scattering was about 1/13 of that of the microemulsion so that the resulting correction was only minor.

Fig. 1 shows SANS data from the lowest, highest, and one intermediate temperature exemplarily.

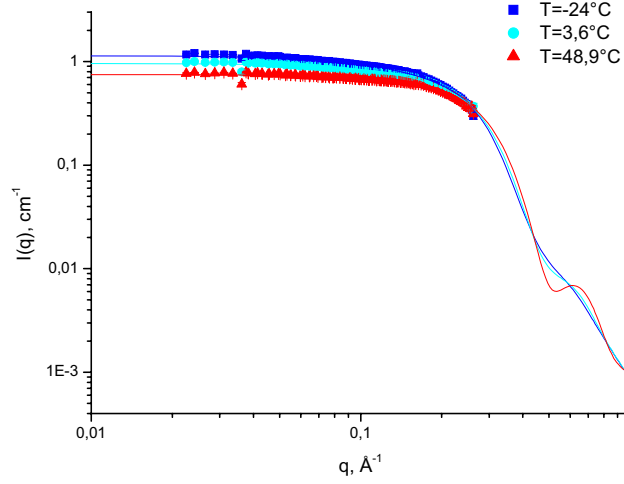


Fig. 1: SANS patterns of the h-PG/d-AOT/d-decalin microemulsion for temperatures -24.0 ± 1 °C, $+3.6 \pm 1$ °C, and $+48.9 \pm 1$ °C. The continuous lines show a fit with the model described below.

The SANS data were fitted by a model combining a Schultz distribution of spheres (characterized by an average radius R_a and a polydispersity p) with a Percus-Yevick type structure factor (characterized by an equivalent hard-sphere radius R_{hs}). The fit parameters shown in Table I indicate that the average radius of particles stays roughly constant while there is a slight increase in polydispersity towards low temperatures.

T, °C	R_a , Å	R_{hs} , Å	p
-24	8,621	9,875	0,22
3,6	8,610	9,220	0,1859
48,9	8,548	8,581	0,1299

Table I: Structural parameters of the microemulsion at three temperatures.

It can be seen that the preliminary result of an extremely small droplet radius could be corroborated. Indeed, the radius is much smaller than estimated in ref. 1, 23 Å. But there, the radius was not measured but concluded from geometrical values, the volume fractions of AOT and PG and the thickness of the AOT layer from literature [2]. The weakness of that approach is obviously that this thickness is not constant when the droplet size is decreased. Rather, the area per AOT headgroup is a constant. While both extrapolations yield the same asymptotic behaviour for large droplets they differ considerably for such small droplets as here.

In retrospect, from the SANS data and the fits the choice of instrument was inappropriate. While the resolution was better than enough, the Q range of 0.25 Å^{-1} was not sufficient to see the characteristic features of the scattering law. We therefore will apply for an experiment involving higher Q values.

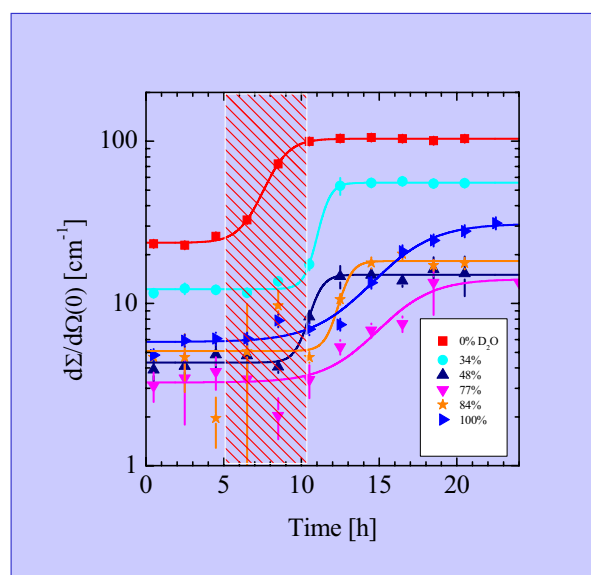
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Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-05-023		
Experiment title:	Kontrast Variation an Fetuin-A/Ahsg - Mineral Aggregaten		
Dates of experiment:	07.04-12.04.2006	Dates of report:	02.06.06
Experimental team: Names	Addresses		
Dr. Wolf-Alexander Heiß	IZKF BioMAT Universitätsklinikum Pauwelsstraße 30 D-52074 Aachen		
Dr. Dietmar Schwahn	IFF, FZ-Jülich, D-52425 Jülich		
Local Contact:	Dr. Dietmar Schwahn		

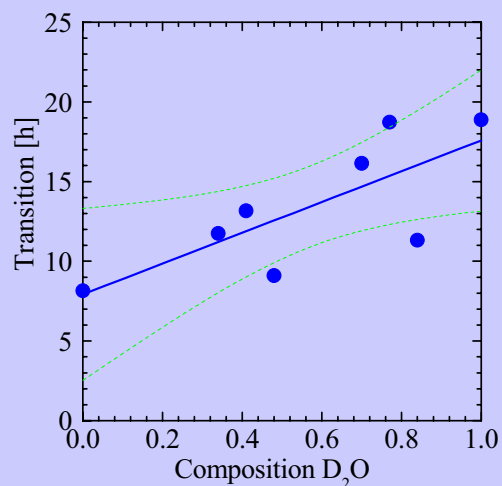
Experimental report text body

Without potent inhibitors, a mineral solid would form in a solution that is supersaturated with regard to calcium and phosphate ions. The plasma protein fetuin-A is capable to buffer a high ion load by formation of colloidal



protein-mineral aggregates, denoted as calciprotein particles (CPP). Price et. al. reported a two-step ripening of the CPPs [1], however the underlying structural transformations remained unclear. In order to understand the structural aspects of inhibition, we studied the CPP growth employing contrast variation.

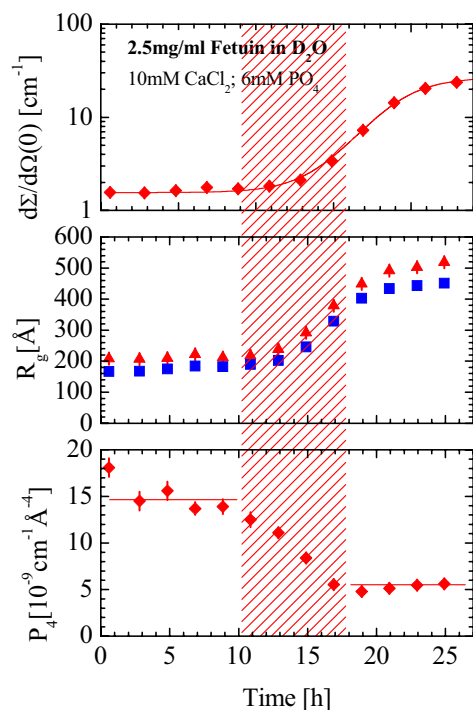
Figure 1 shows the individual time dependent scattering intensities for each contrast. We observed a transformation process from about 5 to 10 hours of incubation indicated by an increase in scattering intensity. At 41% the protein is matched and consequently only the mineral contributes to the total scattering intensity. At 77% the mineral is matched and only the protein is visible.



Interestingly, a linear correlation between the D₂O content and the transformation rate exists (Figure 2, blue line). Despite the variance of this transformation (green lines), a clear trend is visible.

Figure 3 top shows the scattering intensity of a sample containing 2.5 mg/ml bovine fetuin-A, 10 mM CaCl₂ and 6 mM PO₄ in 100% D₂O. In this case the increase in scattering intensity indicating the transformation started after 10 h and ended roughly after 20 h, evidencing again a D₂O caused delay concerning the onset and duration of transformation.

Before the transformation the CPPs have a radius of gyration of 170-200 Å. During transformation their size increases to ~500 Å (figure 3, middle). P₄ is an indicator of the surface extension (figure 3, bottom). We observed a decrease in surface during transformation which is expected from a coarsening mechanism.





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

Proposal number:	KW1-05-024		
Experiment title:	Influence of shear on asphaltene orientation in crude oils		
Dates of experiment:	21.09. - 24.09. 2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink U. Scheven	IFF, FZ Jülich, D-52425 Jülich, Germany Schlumberger Cambridge Research, Cambridge, CB3 0EL, U.K.		
Local Contact:	J. Stellbrink		

Experimental report text body

Asphaltenes are a class of large hydrocarbon molecules comprised of fused poly-aromatic ring cores adorned with short aliphatic chains. In heavy oils they exist as stable colloidal suspensions of micellar structures. Recently Porte et. al. [1] have surveyed the many established experimental results on asphaltene solubility in apolar solvents, and the implications of these results for the mechanisms driving the aggregation processes.

In this experiment we investigated the asphaltene aggregation as a function of temperature and external shear in different types of crude oils using Rheo-SANS. I.e. a Niobium-Couette-cell coupled to a strain controlled Rheowis-Fluid rheometer as sample cell ($d=2 \times 0.5 \text{ mm}$) in radial and tangential geometry. Figure 1 shows the scattering profile without external shear, indicating the existence of two types of aggregates. The primary micelle with an R_g of approximately $30 \text{ \AA}$ and the secondary aggregate with a characteristic length of several thousand Angstroms. One has to keep in mind, that the contrast results only from differences in proton content and density of the different compounds of the crude oil, since all material is protonated. So the overall scattering intensity is, at least a larger Q -vectors, relatively low. In addition the high incoherent background in this Q -regime complicates data analysis.

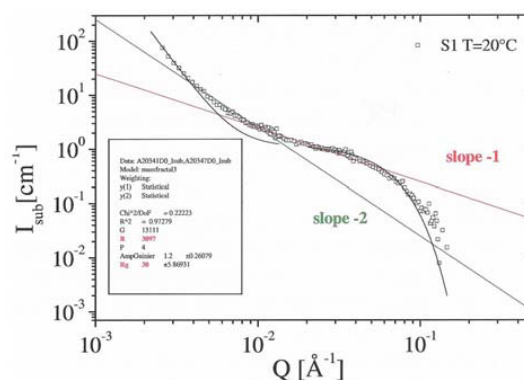


Figure 1: SANS intensity in absolute units versus scattering vector Q for a crude oil without shear.

This incoherent background was estimated from the intensity at the highest Q-vector and finally subtracted from all data sets. Moreover, in tangential geometry the required small sample aperture of 0.5x20mm, which has to fit to the gap size, finally gives that poor data statistics, that we here present only data obtained in radial geometry.

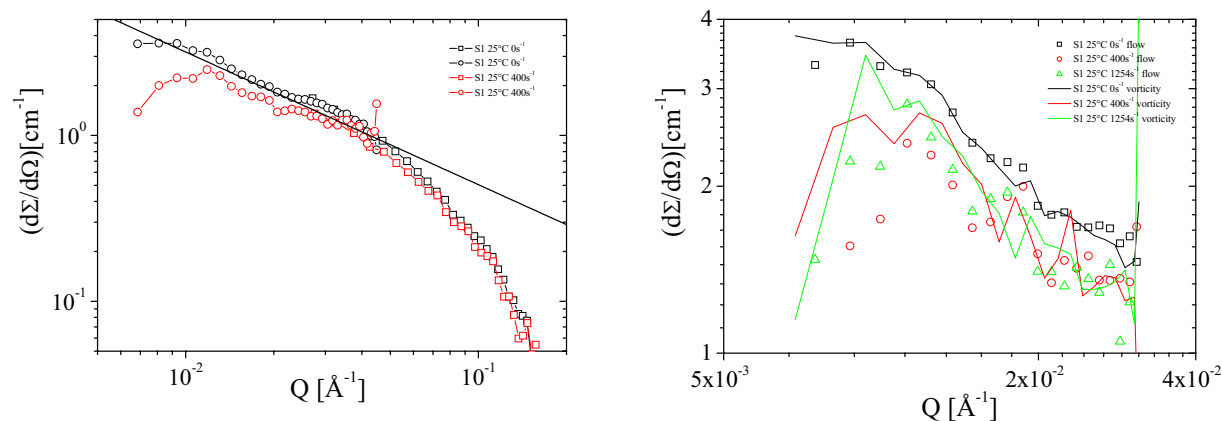


Figure 2: SANS intensity in absolute units for different external shear rates obtained in radial geometry. Left hand side: radial averaged data. Right hand side: Data re-grouped along the flow and the vorticity direction, respectively.

Figure 2 compares data with and without shear. On the left hand side of figure 2 radial averaged data are shown, where only a small effect of external shear is observed. A slightly decreasing scattering intensity at small Q is found, whereas the slope remains constant ≈ 0.8 . On the right hand side we compare data, which were either obtained in flow or vorticity direction. Within experimental error no difference between flow and vorticity direction is observed for all applied shear rates. Also the direct 2D detector images show no indications of anisotropy. In summary, Rheo-SANS [2] is an excellent tool to investigate crude oils, but for a more sophisticated data analysis data of much higher quality are prerequisite, which can only be obtained by considerably longer measurement times.

References:

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

Proposal number:	KW1-05-025		
Experiment title:	SWELLING OF DENSE MICROGEL SYSTEMS		
Dates of experiment:	07.11. – 14.11.2005	Date of report:	23/03/06
Experimental team: Names	Addresses		
ANTONIO FERNANDEZ BARBERO	DEPARTAMENTO DE FISICA APLICADA UNIVERSIDAD DE ALMERIA 04120-ALMERIA SPAIN		
ALBERTO FERNANDEZ DE LAS NIEVES	DEPARTAMENTO DE FISICA APLICADA UNIVERSIDAD DE ALMERIA 04120-ALMERIA SPAIN		
ENRIQUE LÓPEZ CABARCOS	DEPARTAMENTO DE FISICO QUIMICA FARMACEUTICA FACULTAD DE FARMACIA UNIVERSIDAD COMPLUTENSE DE MADRID 28040-MADRID SPAIN		
Local Contact:	MARTINE HEINRICH		

Experimental report text body

Microgels are three-dimensional cross-linked polymer networks immerse in a fluid with dimensions in the colloidal range. In previous works we studied different aspects of thermosensitive, cross-linked poly(N-isopropylacrylamide) [poly(NIPAM)] microgels in D₂O. They present a continuous volume transition from swollen to deswollen states at 34°C. The process is thermoreversible without any kind of hysteresis. We investigated the internal structure of the microgel particles, finding inhomogeneous core-shell structures. The interaction between core and shell was then followed during the volume phase transition [1]. Molecular motions of poly(NIPAM) microgels were investigated in the swollen and collapsed states and during the volume phase transition. More applicated experiments concerning microgel-based biosensors were also investigated using neutron scattering [2].

Ionized VP microgel were also invetigated. When particles are collapsed, phase coexistence and finally a pure crystal phase become apparent, following the expected behaviour for hard spheres. However, *for swollen particles*, the behaviour is fairly different. Even for concentrations higher than the 100% in volume, which means that the swollen microgels have to de-swell due to the external interaction with the rest of the particles, we know by visual inspection that these dense microgels never crystallize. From light scattering experiments we observed structure peaks in the colloidal range shifting towards higher Q values, following a power law $q_{\max} \sim \phi^{1/3}$, which corresponds to neighbouring particles (Figures 1 and 2).

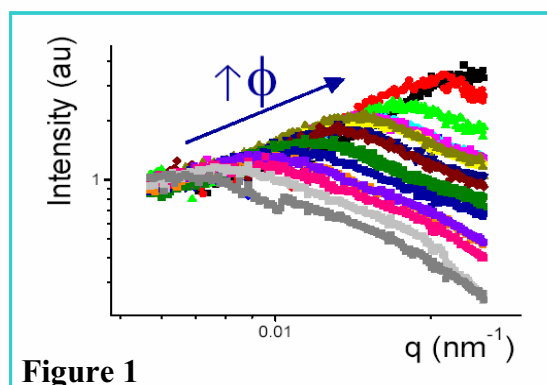


Figure 1

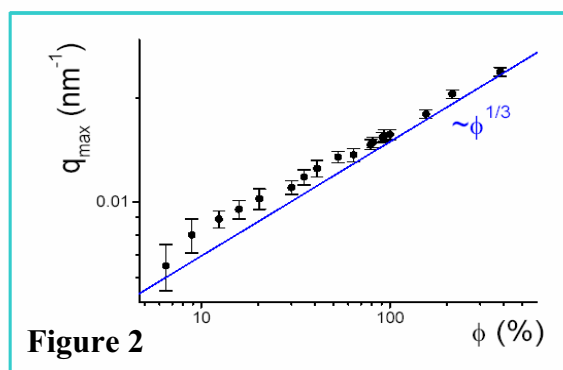


Figure 2

The SANS experiments we are reporting here were designed to monitor the deformation of swollen microgel particles at high particle concentration. 8 different samples were measured at the USANS instrument KWS3 and SANS-KWS1. We measured $I(Q)$ for a swollen VP microgel 0.25% cross-linked with DVB, at different particle concentrations. Figure 3 shows rescaled SANS curves for increasing particle concentration, overlapped on the light scattering curves. A high- Q peak, shown in Figure 4, becomes apparent.

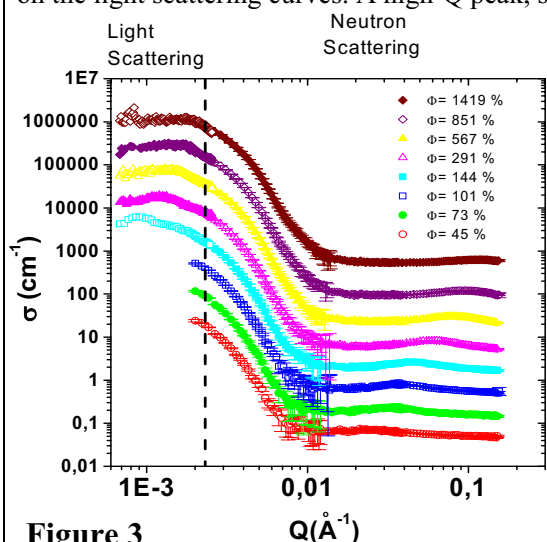


Figure 3

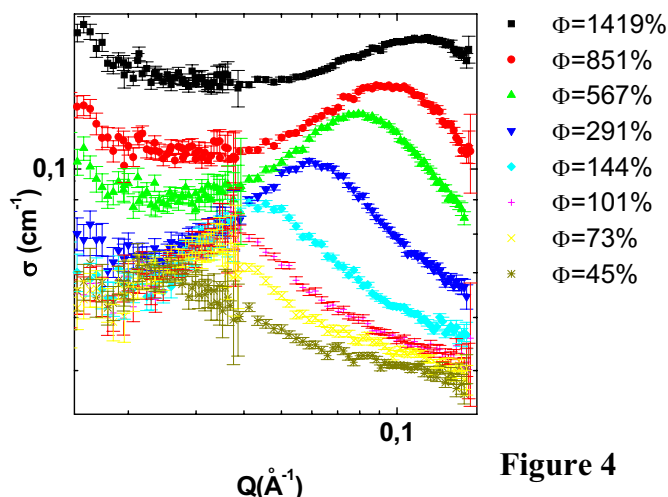


Figure 4

The peak shifts to higher Q values as the particle concentration raises. This indicates an internal structure reducing in size. The nature of this structure has not been identified yet. New experiments are in process using particles with different cross-linker concentrations to estimate if the structure factor change is due to internal particle restructuring or to particle deformation. Additionally, new proposals have been submitted for SANS experiments using dense temperature-sensitive microgels to conclude if the observed structure is charge-induced. The polymer dynamics has been investigated with NMR.

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

Proposal number:	KW1-05-028		
Experiment title:	Exploring the RNA World: adenine-dependent ribozymes		
Dates of experiment:	15.08. – 19.08.2005	Date of report:	08.06.2006
Experimental team: Names	Addresses		
Joseph ZACCAI Yan-Li LI	ILL, Grenoble, France Institut Jacques Monod, Paris, France		
Local Contact:	Dietmar Schwahn		

Experimental report text body

The “RNA World” hypothesis was formulated in the context of the search for the molecular ancestor of living organisms. The central role of RNA in contemporary metabolism includes both informational and catalytic properties, and DNA can be considered as a modified form of RNA, which is more stable in order to conserve and pass on genetic information more efficiently. Despite a number of associated difficulties, the RNA World hypothesis has powerful advantages in its favour. Contemporary transfer RNA contains a rich collection of functionalised bases created by post-transcriptional modification. RNA can thus gain functionality by using catalytic building blocks such as imidazole, thiol, amino, carboxylate groups etc. as cofactors. Nucleotides can acquire, by chemical modification, all the functional groups of amino acids (Maurel and Ninio, 1987). Moreover, primeval nucleotides were not necessarily restricted to the standard ones, as we know them today. Many coenzymes are nucleotide analogues, making it not unlikely that such modified nucleotides played an essential role in prebiotic catalysis.

By using *in vitro* selection, we have recently discovered new hairpin-ribozymes strictly dependent on adenine, *i.e.* RNA enzymes capable of handling adenine as a cofactor for the reversible self-cleavage of an oligonucleotide target. Such studies have evolutionary implications since cofactor assisted ribozymes could be considered as remnants of RNA World ribozymes, handling exogenous prebiotic reactive ligands as cofactors.

Two adenine-dependent hairpin ribozymes (ADHR1, ADHR2) were isolated by *in vitro* selection from a degenerated hairpin ribozyme population (Meli et al., 2003). We characterised the cleavage reaction patterns and kinetics under various conditions and found that both aptamers have Mg^{2+} requirements for adenine-assisted cleavage similar to the wild-type hairpin ribozyme.

The aim of the SANS experiments was to obtain a structural description for the ADHR1 and ADHR2 molecules (each of molar mass 29200 g/mole, containing 85 bases), and their conformational changes upon adenine binding under different conditions. As has been shown previously (Li et al., 1983, Zaccai and Xian, 1988) SANS is a very well-suited method for such low resolution structural studies because of the polyelectrolyte nature of the RNA, and the sensitivity of the scattering patterns to salt conditions and macromolecular hydration.

The following results were obtained during a few days of experiment on KWS-1 spread over 2005 and 2006:

- The RNA samples were aggregated in D₂O solvents and the data could not be exploited.
- Good, reproducible data were obtained for both ADHR1 and ADHR2, and two mutants in H₂O buffered solvent with 100mM NaCl. An analysis of the forward scattering on an absolute scale and of the radius of gyration in the Guinier approximation as well as the general tendency of the $I(Q)$ dependence indicated the RNA molecules, in both cases, are in the form of elongated dimers compatible with two-hairpin conformations arranged in a parallel or antiparallel configuration.
- A time course experiment was designed following the slow kinetics of adenine-dependent cleavage, observed by gel chromatography. For both ADHR1 and ADHR2, the scattering curve did not change after addition of adenine over a 24h period. This indicated that the dimer structure was unaltered, and that under non-denaturing conditions the cleaved RNA products remained in association.

The analysis of the scattering curves is now continuing, by using model fitting SAS programs in order to obtain a more refined view of the three-dimensional structure of the RNA dimer in solution, and correlating the results with biochemical data from various mutants. A publication is in preparation for *Nucleic Acids Research*.

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

Proposal number:	KW1-05-031		
Experiment title:	Structural study of a novel class of contrast agents for using in Magnetic Resonance Imaging techniques		
Dates of experiment:	07 th -10 th November 2005	Date of report:	07 st December 2005
Experimental team: Names	Addresses		
Prof. Luigi Paduano	Università degli Studi di Napoli "Federico II", Dipartimento di Chimica, Complesso universitario di M.S. Angelo, Via Cinthia, 80126 Napoli, Italy		
Dr Gaetano Mangiapia	Università degli Studi di Napoli "Federico II", Dipartimento di Chimica, Complesso universitario di M.S. Angelo, Via Cinthia, 80126 Napoli, Italy		
Mauro Vaccaro	Università degli Studi di Napoli "Federico II", Dipartimento di Chimica, Complesso universitario di M.S. Angelo, Via Cinthia, 80126 Napoli, Italy		
Local Contact:	Dr. Aurel Radulescu		

Experimental report text body

The purpose of this research project has been the development of peptide containing supramolecular amphiphilic aggregates as selective nanocarriers for high-relaxivity Magnetic Resonance Imaging (MRI) contrast agent. Our aggregates were formed by the bioactive peptide CCK8 (the bio-specific probe) able to target the aggregates on cholecystokinin receptors that are known to be overexpressed by many tumours, and a chelate molecule (DTPAGlu) able to carry a large number of Gd ions (contrast agent) to highlight the presence of such tissues; both the moieties were bound to a hydrophobic double-tail (18 carbon atoms). All the molecules have been synthesized at University of Naples, "Federico II" – Interuniversity Center for Bioactive Peptides and are named as (C18)₂DTPAGlu and (C18)₂CCK8. These surfactant molecules are capable of forming aggregates of different size and shape, such as micelles and vesicles, in aqueous solution by varying the method of preparation and the environmental conditions in solution such as pH, ionic strength and temperature. We have realized a detailed study of structural evolution of the aggregates by varying pH since the increasing interest in current clinical diagnostic for pH responsive MRI contrast agents.

Figure 1 shows some of the SANS data obtained for the systems (C18)₂DTPAGlu–D₂O and (C18)₂DTPAGlu–(C18)₂CCK8–D₂O at different pH values. Correspondent systems containing Gd³⁺ have also been analyzed. The figure shows clearly the evolution of supramolecular aggregates with the pH from micelles to vesicles or bilayer aggregates. At pH 7.4 the scattering intensity shows at low q values a q⁻² decay typically of the double layer scattering, but the scattering profile also shows the presence of a rising peak in the intermediate q range (0.02 < q < 0.06 Å⁻¹) that are originated by the presence of micelles. At lower pH values, as pH 3, the cross-scattering section shows a clear q⁻² decay in whole the q range analyzed, indicating the presence of only bilayer structures in the system. By decreasing pH the carboxylic groups present in the DTPAGlu moiety are protonated and the formation of low curvature and large aggregates such as vesicles or in general bilayer is advantaged. In order to extract quantitative parameters from SANS data we have expressed the scattering cross section as a sum of a term expressing the scattering of sheets and a term proper of the scattering of cylinders,

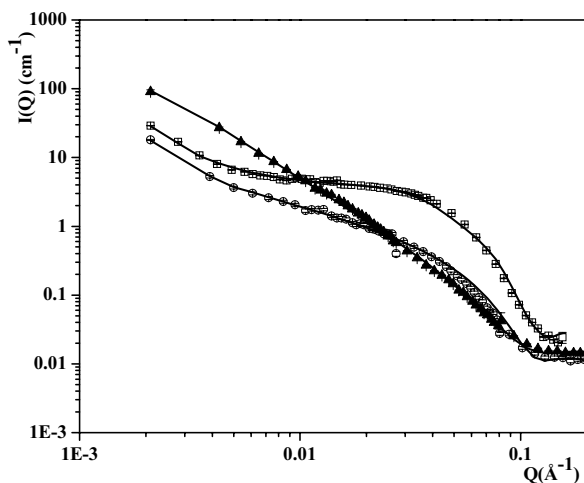
neglecting the interference term between the two kinds of aggregates

$$\frac{d\sigma}{d\Omega}(q) = \left[\int_0^{\pi/2} \frac{\sin^2\left(\frac{ql \cos \phi}{2}\right)}{\left(\frac{ql \cos \phi}{2}\right)^2} \frac{9 \left[j_1(qR \sin \phi) \right]^2}{(qR \sin \phi)^2} \sin \phi d\phi \right] (\rho_{cyl} - \rho_0)^2 \pi R l + 2\pi (\rho_{ves} - \rho_0)^2 S \tau^2 \frac{1}{q^2} \frac{\sin^2\left(\frac{q\tau}{2}\right)}{\left(\frac{q\tau}{2}\right)^2} + \left(\frac{d\sigma}{d\Omega} \right)_{inch}$$

where R and l are respectively the radius and the height of cylinders, while S is the area of sheet per unit volume of sample. Table 1 shows the results obtained through the fitting of previous equation to the experimental data. Assembled molecules form cylinders with a quite large aggregation number (~ 100). The surfactants composing our micelles are disposed with their alkyl tails parallel to cylinder radius and this latter has been evaluated to be nearly the same to the length of molecule.

SANS measurements have also allowed getting the value of the vesicular thickness that ranges between 50 Å and 70 Å depending pH value. Revealing the formation of more compact aggregates as the pH is decreased.

Figure 1. – SANS data obtained at 25°C for the following systems:



∇ (C18)₂DTPAGlu (0.00079 mol kg⁻¹)- (C18)₂L5CCK8 (0.00038 mol kg⁻¹) – D₂O at pH 7.4

– (C18)₂DTPAGlu (0.00063 mol kg⁻¹)- (C18)₂L5CCK8 (0.00037 mol kg⁻¹) – D₂O at pH 4.5

7(C18)₂DTPAGlu (0.00063 mol kg⁻¹)- (C18)₂L5CCK8 (0.00038 mol kg⁻¹) – D₂O at pH 3

Curves presented have been obtained from the fitting of the model described in the text to the experimental scattering cross sections.

Systems	pH	N _{agg}	R(Å)	h(Å)	τ(Å)
(C18) ₂ DTPAGlu (0.00079 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00038 mol kg ⁻¹)- D ₂ O	7.4	125±15	39±3	198±39	70±5
(C18) ₂ DTPAGlu (0.00081 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00036 mol kg ⁻¹)- D ₂ O (not extruded)	7.4	102±10	38±4	108±23	71±4
(C18) ₂ DTPAGlu (0.00063 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00037 mol kg ⁻¹)- D ₂ O	4.5	771±80	36±2	710±60	58±3
(C18) ₂ DTPAGlu (0.00063 mol kg ⁻¹) – (C18) ₂ L5CCK8 (0.00038 mol kg ⁻¹)- D ₂ O	3				47±5
(C18) ₂ DTPAGlu(Gd) (0.00079 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00037 mol kg ⁻¹) - D ₂ O	7.4	110±17	35±3	203±33	72±5
(C18) ₂ DTPAGlu(Gd) (0.00063 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00039 mol kg ⁻¹)- D ₂ O	4.5	723±65	34±2	741±82	63±10
(C18) ₂ DTPAGlu(Gd) (0.00063 mol kg ⁻¹)- (C18) ₂ L5CCK8 (0.00032 mol kg ⁻¹)- D ₂ O	3				51±6

Table 1. Structural values obtained for micelle aggregates and vesicles, gotten through the fitting of the model described in the text to the experimental data. The symbols presented are:

N_{agg} Aggregation number of cylindrical micelles.

R Radius of the cylinders

l Height of the cylinders

τ Vesicular thickness



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

Proposal number:	KW1-05-032		
Experiment title:	Structure of gels formed by pH-responsive core-shell-corona aqueous micelles		
Dates of experiment:	29.09.2005 – 03.10.2005	Date of report:	25.03.2006
Experimental team: Names	Addresses		
Bernard Leyh Nicolas Willet Jean-François Gohy Robert Jérôme	Laboratoire de Dynamique Moléculaire, Département de Chimie, Université de Liège, B-4000 SART-TILMAN C.E.R.M., Département de Chimie, Université de Liège, B-4000 SART-TILMAN CMAT, Université Catholique de Louvain, B-1348 LOUVAIN-LA-NEUVE C.E.R.M., Département de Chimie, Université de Liège, B-4000 SART-TILMAN		
Local Contact:	Dr. Martine Heinrich		

Experimental report text body

The self-assembling of triblock copolymers leads to novel micellar architectures that can be sensitive to external stimuli.¹⁻⁷ Their behaviour in selective solvents still needs to be studied in detail. In this project, self-assembling of triblock copolymers of polystyrene₂₀₀-*b*-poly(2-vinylpyridine)₁₄₀-*b*-poly(ethylene oxide)₅₉₀ has been further investigated. This copolymer self-assembles into pH-responsive core-shell-corona micelles in aqueous solution.^{4,5} It also leads to the formation of a gel at 8 w/w% in a DMF/water mixture. A soft-to-hard gel transition is observed upon acidification.

Due to time limitations and to the low scattering signal of our systems, we have focused on the analysis of the structure factor in the vicinity of the overlap concentration, c^* , at neutral and acidic pH. Microscopy experiments,^{4,5} as well as our previous SANS experiments,⁸ show that the poly(2-vinylpyridine) shell thickness increases approximately by a factor of two when the initially neutral pH is decreased to a value of about 5. This also induces a swelling of the external PEO corona as proven by both dynamic light scattering and SANS.⁸ As a result, the overlap concentration is observed to decrease upon decreasing pH, from about 3 w/w % in neutral solution to 0.6 w/w % under acidic conditions. We performed a systematic study of the evolution of the structure factor as a function of the copolymer concentration and as a function of pH. The analysis of the results should provide us with information on the intermicellar interactions.

The following experiments have been performed: (i) measurement of the scattering cross section for neutral aqueous solutions of polystyrene₂₀₀-*b*-poly(2-vinylpyridine)₁₄₀-*b*-poly(ethylene oxide)₅₉₀ at increasing copolymer concentrations in the 2.0 – 4.0 w/w % range; (ii) similar measurements in acidic solutions corresponding to the complete protonation of the poly(2-vinylpyridine) block; the investigated copolymer concentrations were in the 0.4 – 0.8 w/w % range.

The macroscopic scattering cross section at increasing copolymer concentrations under neutral conditions could be well described using the Percus-Yevick (PY) hard sphere model,⁹ as shown in Figure 1. The total scattering intensity is assumed to be proportional to the product of the form factor and of the PY static structure factor. The fitted parameters are displayed in Table 1.

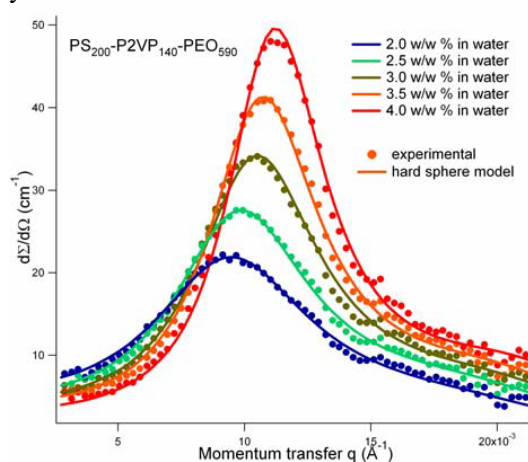


Figure 1 Scattering cross sections under neutral pH conditions

[PS- <i>b</i> -P2VP- <i>b</i> -PEO] (w/w %)	Volume fraction Φ	Sphere diameter σ (Å)	Radius of gyration R_g (Å)
2.0	0.19	590	115
2.5	0.23	590	110
3.0	0.27	570	110
3.5	0.30	570	110
4.0	0.34	560	108

Table 1 Fitted parameters from the experimental data of figure 1 and the Percus-Yevick hard sphere model

When the copolymer concentration is raised, the first peak of the structure factor becomes progressively larger and narrower, indicating a tendency to a longer range ordering of the micellar solution. A moderate decrease of σ takes place indicating that one is approaching the overlap concentration. The product of the copolymer concentration by σ^3/Φ remains constant within experimental errors.

A similar data handling has been applied to the cross sections recorded at lower pH. In agreement with our previous SANS analysis of the form factor,⁸ the global sphere diameter is increased by a factor of approximately 2 and is now in the 1000-1200 Å range. A significant steady decrease of σ is observed when the copolymer concentration is raised, as a result of the overlap between micelles. To reach a more realistic picture of the interactions between charged micelles in acidic solution, we are now performing an analysis based on the rescaled mean spherical approximation.¹⁰

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

Proposal number:	KW1-05-033		
Experiment title:	Drug-induced variations of the microviscosity, shape and size of lipid bilayers: interaction of cholesterol and methyl- β -cyclodextrins with DMPC and DPPC liposomes		
Dates of experiment:	28.10.2005 – 31.10.2005	Date of report:	26.03.2006
Experimental team: Names	Addresses		
Mohamed Ali Bahri Angeliki Grammenos Maryse Hoebeke	Laboratoire de Physique Biomédicale, Département de Physique, Université de Liège, B-4000 SART-TILMAN		
Jean-Pierre Gaspard	Laboratoire de Physique de la Matière Condensée, Département de Physique, Université de Liège, B-4000 SART-TILMAN		
Bernard Leyh	Laboratoire de Dynamique Moléculaire, Département de Chimie, Université de Liège, B-4000 SART-TILMAN		
Local Contact:	Dr. Martine Heinrich		

Experimental report text body

Liposomes resulting from the self-assembling of phospholipids are important models of biological membranes because their spherical bilayer structure separates two aqueous media, like the cell plasmic membrane.^{1,2} Unilamellar vesicles are particularly relevant, also because they can be used as drug delivery agents.

The aim of this project is to investigate the interaction between liposomes, resulting from the self-assembling of amphiphilic dimyristoylphosphatidylcholine (DMPC) or dipalmitoylphosphatidyl-choline (DPPC) chains, and molecules like cholesterol and cyclodextrins. The addition of drugs can affect the membrane microviscosity and the structural parameters of the liposomes, both effects being possibly linked. A better understanding of the drug action mechanism requires therefore quantifying these two key-observables. Our strategy consists in combining two experimental approaches: SANS to derive the size parameters of the liposomes and ESR (Electron Spin Resonance) to probe the microviscosity.

The effect of cholesterol, at various concentrations, on the DMPC liposomes has been studied quantitatively by ESR at room temperature. The membrane saturation in cholesterol is made progressively from the head group to the centre of the bilayer. The mechanism by which the microviscosity is increased involves the association of cholesterol with fatty acid side chains, reducing their rotational mobility. Cyclodextrins are cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic central cavity. Some cyclodextrins extract cholesterol from biological membranes.³ They have also been observed to release some liposome-encapsulated drugs without disrupting the vesicles.⁴ In the present work, we consider the interaction between randomly methylated β -cyclodextrins, denoted Rameb, and cholesterol-containing DMPC or DPPC liposomes. One essential question is whether the cholesterol extraction by Rameb is accompanied or not by the disruption of the liposomes.

The following experiments have been performed: (i) measurement of the form factors of the DMPC liposomes in D₂O with increasing concentrations of Rameb (0 – 0.03 mol/L range) and at two temperatures (14°C and 34°C), i.e., below and above the gel-liquid transition temperature; (ii) measurement of the form factors of cholesterol-containing (30%) DMPC liposomes, in the same Rameb concentration range and at 14°C and 34°C; (iii) measurement of the form factor of cholesterol-containing DPPC liposomes without and with Rameb (0.03 mol/L). Typical data are displayed in Figure 1. They illustrate the effect of cholesterol insertion followed by its extraction by the Rameb cyclodextrin.

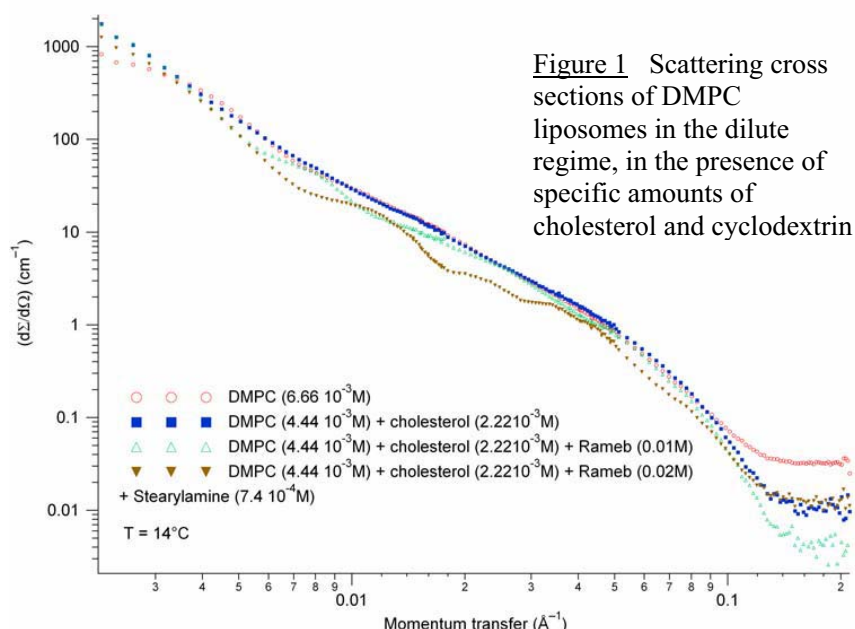


Figure 1 Scattering cross sections of DMPC liposomes in the dilute regime, in the presence of specific amounts of cholesterol and cyclodextrin

These data show that the liposomes survive the cholesterol extraction by the Rameb cyclodextrin. An analysis of the radii of gyration (R_g) leads to the following conclusions.

- (i) Progressive addition of Rameb in the absence of cholesterol leads to an increase of R_g , starting from 460 Å, followed by a rapid levelling off (around 550 Å) which is reached already at a Rameb concentration between 0.005 mol/L and 0.01 mol/L. This confirms that the cyclodextrin molecules get adsorbed, possibly under dynamic equilibrium conditions, onto the liposome external layer.
- (ii) This increase is somewhat larger below the transition temperature.
- (iii) The insertion of cholesterol into the lipidic part of the double-layer leads logically to a substantial increase of R_g , which then reaches 700 Å. Addition of increasing amounts of Rameb at 14°C to the cholesterol-containing liposome solution leads first to a further increase of R_g and then to a decrease without reaching the values observed in the absence of cholesterol. A possible mechanism is that Rameb gets first adsorbed, thus increasing R_g , then extracts cholesterol before being desorbed and replaced by free cyclodextrin molecules, so that R_g decreases. The fact that the radius of gyration remains larger than without cholesterol is an indication that cholesterol extraction is not complete under our concentration conditions.

This analysis will be completed by fitting the experimental scattering cross sections to a model taking into account the different contrasts associated with the internal structure of the liposomes with and without cholesterol and Rameb.⁵⁻⁷ This will provide us with the relevant structural parameters.

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

Proposal number:	KW1-05-034		
Experiment title:	Firing technology for medieval ceramic production in the Salento region (Italy)		
Dates of experiment:	05-11-2006	Date of report:	02-03-2006
Experimental team: Names	Addresses		
Alberto Botti Armida Sodo Maria Antonietta Ricci	Univ. Roma TRE, Dip. di Fisica "E. Amaldi", via della vasca navale 84, 00146 Roma (Italy)		
Marco Leo Imperiale Paul Arthur	Univ. Lecce (Italy)		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

The early medieval production of the Byzantine kiln of "Cantiere Mitello" by Otranto, a small harbour on the Apulian Adriatic sea, has been investigated through SANS measurements.

We have collected the small angle scattering patterns of 41 samples which belong to five different groups: namely three types of amphorae with different shapes, a typology of painted amphorae and a series of tableware. All the sherds are coeval and dated back to the VII-VIII century AD.

The samples did not undergo a specific preparation beside a micro-destructive drawing of a tiny amount of ceramic powder. This has been set down of a tape film in manner to form a thin layer. The tape film has been measured separately and subtracted as sample holder.

The small thickness of the samples avoided distortion of the curves caused by multiple scattering processes. Moreover the data have been collected on a Q range from 2×10^{-3} to 1.6×10^{-1} , well below the upper cut off of the fractal behaviour (from DKD and KWS3 measurements estimated to be $\sim 1-10 \mu\text{m}$) [1]. The high Q tail shows indeed on a double logarithmic scale a linear behaviour (see Figure 1), and the data can be fitted with a simple function of the type

$$I(Q) = I_0 Q^{-d} + BG$$

Where I_0 is a prefactor, BG is the level of the incoherent scattering and d is the fractal dimension of the aggregates of the ceramic.

The results of the fitting procedure are plotted in Figure 2 as bars of different colour. In the x axis is reported the fractal dimension, while on the y axis only a dummy value, always the same for all the samples. This graph shows the possible gathering of the d values around a specific value for different typology of objects.

Following the procedure described in Ref [2], the aim of this study was to assess whether the production of “Cantiere Mitello”, one of the few examples of Byzantine kilns in Italy [3], adopted different firing strategies according to the final product. A further question concerned the differences between the technologies used by the coeval potters of the west coast, settled in Campania in Miseno and Cuma and more connected to Rome, and that one used on the east coast and facing the Eastern Empire: they had distinct customers and end markets.

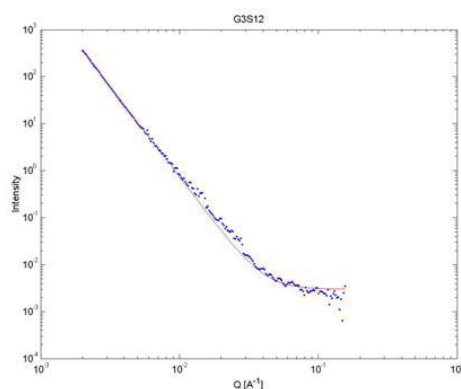


Figure 1

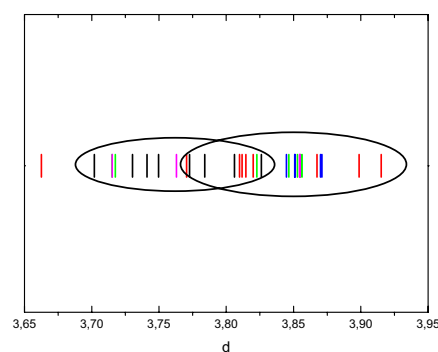


Figure 2

From previous experiments it has been established that once the mineralogical composition has been fixed, d linearly depends on the maximum firing temperature and it is independent on heating rate. [2]

From Figure 2, this implies that the tableware (black bars) have been fired at lower temperature compared to the amphorae (coloured bars).

Moreover, all the samples from Otranto have been fired at a temperature higher than that used in the kiln of Miseno and Cuma. At this stage, the latter conclusion must be considered only as an hypothesis, because of the correlation of the absolute value of d with the phase content of the sherds. This hinders, as long as the mineralogical composition of the Otranto samples is not known (TOF-ND measurements are scheduled for June 2006), a straightforward comparison of the two productions.

[1] A. Botti, Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor, p. 343 (2004).

[2] A. Botti, M. A. Ricci, G. De Rossi, W. Kockelmann, A. Sodo, J. Archaeological Science, **33** 307 (2006).

[3] M. Leo Imperiale, Proceedings of: III Congresso Nazionale di Archeologia Medievale (Salerno 2-5 October 2003)



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

Proposal number:	KW1-05-035		
Experiment title:	Conformation of the cytoplasmic part of the trasducer		
Dates of experiment:	26.08.2005	Date of report:	28.03.2006
Experimental team: Names	Addresses		
Ivan Budyak	Forschungszentrum Jülich, IBI-2		
Vitaliy Pipich	Forschungszentrum Jülich, IFF		
Georg Büldt	Forschungszentrum Jülich, IBI-2		
Judith Klein-Seetharaman	Forschungszentrum Jülich, IBI-2; University of Pittsburgh, USA		
Local Contact:	Dr. D. Schwahn, Dr. V. Pipich		

Experimental report text body

The SANS measurements were done at the KWS-I instrument at the FRJ-2 research reactor (Research Center Jülich, Germany). A neutron wavelength of $\lambda=7 \text{ \AA}$ with sample-to-detector distances of 2 and 4 m were used to get a range in scattering vector $Q=2\pi/\lambda$ values of 0.01 to $0.2 \text{ \AA}^{-1}$. Protein samples containing 2 and 7.5 mg/ml pHtrII-cyt in dPBS and 5 mg/ml pHtrII-cyt in dPBS + 4M KCl were analyzed at room temperature in quartz cells with 1-mm path lengths. The data were corrected for the detector efficiency, the scattering from the empty cell and solvent, and then radially averaged and calibrated in absolute units by a plexiglas secondary standard. Scattering curves were fitted using the approximation proposed by Beaucage (Beaucage, *J.Appl. Cryst.*, 1996) which combines both the Guinier regime (Guinier and Fournet, *Small Angle Scattering of X-rays*. 1955) and the fractal regime:

$$I(Q) = G \exp(-R_g^2 Q^2/3) + P [\text{erf}(R_g Q/\sqrt{6})]^3 / Q \quad (1)$$

where R_g is the radius of gyration, G is the Guinier prefactor

$$G = \Phi(1-\Phi)V\Delta\rho^2 \quad (2)$$

and P is the amplitude of the fractal part

$$P = \Phi(1-\Phi)\pi^2 r^2 V \Delta\rho^2. \quad (3)$$

Using this equation, the following features can be derived from the curve: (i) the zero Q intercept gives the particle volume if the concentration is known, (ii) the slope of the Guinier region is equal to $-R_g^2/3$ and therefore gives the particle size, (iii) the slope of the mass fractal dimension indicates the shape, (iv) and the Porod region gives the surface area and surface fractal dimension (Beaucage, *J.Appl. Cryst.*, 1996).

We used SANS to complement our observations from analytical gel-filtration and crosslinking experiments, that the cytoplasmic part of the transducer II from *Natronobacterium pharaonis* (pHtrII-cyt) is predominantly monomeric in PBS (Dulbecco and Vogt, *J.Exp.Med.*, 1954) and dimeric in PBS + 4 M KCl. All measurements were carried out in buffers prepared in D_2O to improve the signal:noise ratio.

The concentration-normalized experimental data are plotted in Fig.1 for pHtrII-cyt in dPBS as open circles (○) and in dPBS + 4M KCl as open squares (□). In both cases, the scattering intensity $I(Q)$ follows the scaling law Q^{-1} over a wide Q range of 0.03 to 0.2 $\text{\AA}^{-1}$ (Fig. 1, dashed line). The observation of a $I(Q) \sim Q^{-1}$ dependence is consistent with an elongated (rod-like) shape of pHtrII, both in dPBS and in dPBS + 4M KCl and can be approximated with a cylinder.

The volume fraction of protein Φ was calculated from the ratio between the pHtrII-cyt concentration and the protein density in H_2O , $\Phi = c/d_p$; the volume of the cylinder was assumed to be equal to the molecular volume of protein $V = M/N_a/d_p$. From Eq. 2 and 3, the length and the radius of the protein molecules can be calculated according to:

$$L = \pi G/P \quad (4)$$

$$r = \sqrt{(V/\pi/L)} \quad (5)$$

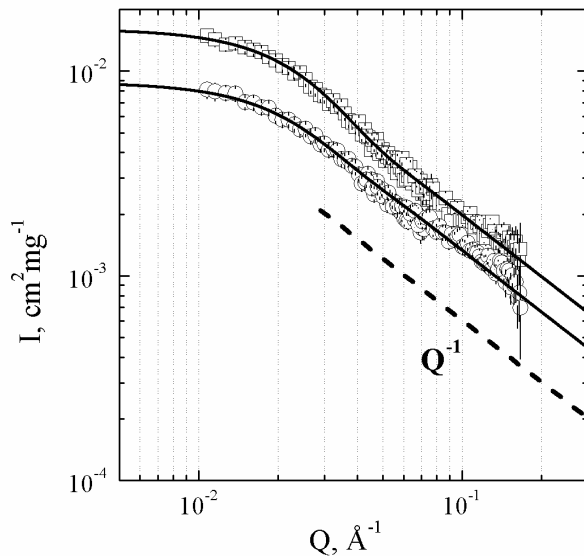
The values for the length and radius obtained for the pHtrII-cyt molecules in dPBS buffer were $L_{\text{PBS}} = 202 \pm 5 \text{ \AA}$ and $r_{\text{PBS}} = 7.2 \pm 0.3 \text{ \AA}$, respectively. From these values, the radius of gyration R_g was calculated based on the cylinder model. For a cylinder of length L , radius r and unifrom mass distribution, R_g is given by:

$$R_g^2 = L^2/12 + H^2/2 \quad (6)$$

For pHtrII-cyt, this gives a radius of gyration of $R_g = 58.5 \text{ \AA}$. This value is similar to the radius of gyration value obtained directly from Eq. 1, which was $50.8 \pm 0.8 \text{ \AA}$. The overall shape of the SANS spectrum measured in dPBS + 4M KCl was essentially identical to that observed in dPBS buffer alone. In contrast, the reduced zero intensity G :

$$G/c = 1/d_p V \Delta\rho^2 \quad (7)$$

in the presence of 4 M KCl in dPBS buffer was 1.8 higher than the zero intensity G observed in dPBS buffer alone. This increase can either result from a change in the particle volume V and/or the square of the scattering contrast. If we assumed a constant volume ($V_{\text{SALT}} = V_{\text{PBS}}$), the scattering length density of HtrII-cyt in D_2O would be $\rho_p = 2.3 \times 10^{10} \text{ cm}^{-2}$. This value would be much lower than expected for proteins in D_2O and could only be accounted for if the protein would bind hundreds of K^+ ions. On the other hand, if we assumed a constant scattering length density ($\rho_p^{\text{SALT}} = \rho_p^{\text{PBS}}$), the particle volume would increase by a factor of 12. Thus, the result indicates that the increase in zero intensity must result from a combined increase in particle volume and change in scattering contrast. In particular, if we assume $V_{\text{SALT}} = 2V_{\text{PBS}}$, the scattering length density of pHtrII-cyt in dPBS + 4 M KCl becomes $\rho_p = 3.22 \times 10^{10} \text{ cm}^{-2}$. This value is very close to the value typically observed for proteins in D_2O . The decrease of the scattering length density from $4.37 \times 10^{10} \text{ cm}^{-2}$ in dPBS to $3.22 \times 10^{10} \text{ cm}^{-2}$ in the presence of 4 M salt suggests exclusion of D_2O from the protein's interior, either by "tightening" of the structure and/or by binding of K^+ ions.



The volumes and scattering length densities from the above calculations were used to approximate the experimental scattering curve by using Eq. 1. The resulting curve is shown in Fig. 1. The molecule length and radius were calculated according to Eq. 4 and 5. The length and radius increased from $L_{\text{PBS}} = 202 \pm 5 \text{ \AA}$ and $r_{\text{PBS}} = 7.2 \pm 0.3 \text{ \AA}$ to $L_{\text{SALT}} = 248 \pm 7 \text{ \AA}$ and $r_{\text{SALT}} = 9.1 \pm 0.4 \text{ \AA}$. When calculating the radii of gyration using these values and comparing them to the direct calculation using Eq. 1, a significant difference between $R_g = 56 \pm 1 \text{ \AA}$ (obtained from Eq. 1) and $R_g = 72 \text{ \AA}$ (calculated from Eq. 6) was observed. Since the experimental value is less than the theoretical value, the mass is either concentrated at the center of the cylinder or the cylinder is not ideal, i.e. the diameter at the center is larger than that on the edges. Thus, there is non-homogeneous mass distribution within the pHtrII-cyt dimer molecule in the presence of 4 M KCl in contrast to the pHtrII-cyt monomer in dPBS alone, which displayed uniform mass distribution.



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

Proposal number:	KW1-05-036		
Experiment title:	Kinetics and dimensions of polymeric stabilised zirconia sols. Sol synthesis for microporous zirconia membranes with power plant gas separation as application		
Dates of experiment:	15.08.2005 11.12.2005	Date of report:	13.03.2006
Experimental team: Names	Addresses		
G.J.W. van der Donk Dr. Tim Van Gestel Dr. Wim Pyckhout-Hintzen	Forschungszentrum Jülich, IWV1 Forschungszentrum Jülich, IWV1 Forschungszentrum Jülich, IFF		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

Experimental report text body

Due to the Kyoto protocol, increasing intensive research is in progress to separate CO₂ from the power plant exhaust. This can be performed at the 'End of Pipe' (post combustion) or with new concepts such as pre combustion (H₂/CO₂) or oxy-fuel (N₂/O₂) processes. Inorganic microporous membranes benefits from the mechanical, thermal and chemical stability above carbon based polymers. Present inorganic microporous membranes with high permeation are based 30 nm thin layers of silica with particles less than 10 nm¹. Silica microporous membranes lack the stability in humid conditions at high temperate. Zirconia is known for its thermal stability. These microporous membranes with pore size smaller than 1 nm can be applied in gas separation applications.

However, the polymeric zirconia or titania synthesis is more complex than the polymeric silica sol due to the fast kinetics of the hydrolysatation process. The zirconia sol is a polymer, fractionated, and therefore the sol can be idealised as a sphere. Zirconia sols have been analysed with dynamic light scattering resulting in estimated/calculated particle size diameter of 3-10 nm. However, neither SAXS or DLS could give us accurate information on the mass and surface fractal.

Van Gestel has prepared three different polymeric sols, one titania based sol and two zirconia based sols. One of the zirconia sols has been synthesised with a bimodular particle size distribution (Figure 1). The cluster structure (shape) of these sols can only be studied with small angle diffraction. 0.5 wt% diluted zirconium and titanium sols have been prepared in propanol. These sols are diluted for good coating behaviours and fulfil the Guinier approximation requirement of diluted particles. The sol is based on a polymer chain of a metal ion with acetylacetone and propyl groups. The presence of propyl groups and propanol as solvent resulted in a calculated low contrast, which can result in significant noise in the scattering intensity. Deuterated ethanol (EtOH-d₆) was added in a 50/50% weight ratio to increase the contrast. Standard SANS procedure was followed for measuring the three samples including a solvent (propanol- EtOH-d₆) and empty quartz cells.

The scattering intensities of both zirconium and titanium sols with average sol size (DLS) of 5 nm were rather low and resulted in a high noise/signal ratio. The log-log plot intensity and scattering vector, the Porod plot, of the bi-modal zirconium sol resulted in high noise at relative large scattering vector. (Figure 2). But, a clear trend could be observed in the small scattering vector region. This indicates a mass fractal dimensional of about 1.3 when we assume that the particles are monodispersed. It is assumed that the dimensional fractal is stable due to the diffusion limitation of the cluster-cluster aggregation². The dimensional fractal can be dependent on the water and acid content in the sol. This behaviour is not studied for these samples, yet. Therefore, the value of dimensional fractal can only indicate a sparser appearance of the polymer structure. The log intensity – log Q^2 plot presented the Guinier region where the sol size could be determined (Figure 3 and Figure 4). The bi-modal zirconium sol size distribution is confirmed with SANS. Clearly, two slopes could be identified resulting in a particle size of 12(3) and 35 (5) nm. The curve is a combination of both slopes. It is hard to distinguish both slopes, the error is estimated. DLS suggest peaks at 6 and 60 nm (Figure 1). A second SANS beam time was approved. Sols with higher concentration will be synthesised to increase the intensity. Four sols have been prepared with a higher concentration ~15wt% to obtain a higher contrast. The new samples are not diluted with EtOH-d₆ to maintain high concentrated samples. A zirconia and titania sols have been prepared with capronic acid as catalyser and another zirconia and titania have been prepared with diethyl-amine as catalyser. Unfortunately, only the last sample resulted in an acceptable result to obtain the particle size of 4 nm.

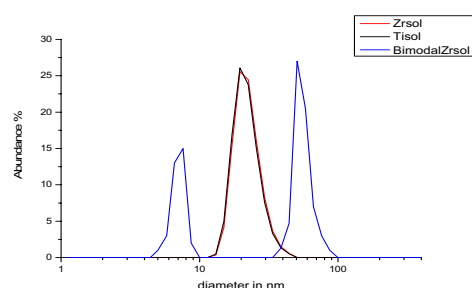


Figure 1 Sol size distribution of zirconia and titania based sols.

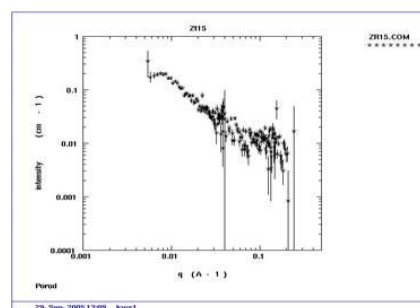


Figure 2 Porod plot of zirconium sol #Zr15

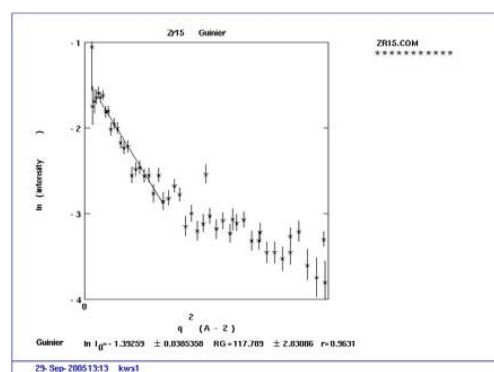


Figure 3 Guinier plot of zirconium sol #Zr15 with steep slope

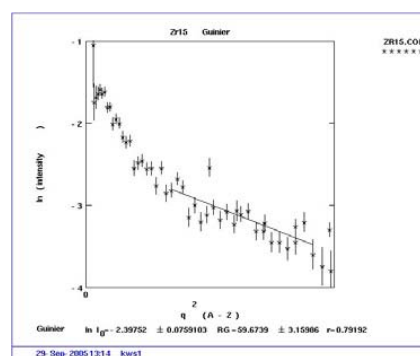


Figure 4 Guinier plot of zirconium sol #Zr15 with flat slope

SANS measurements confirms the bimodal particle size of the zirconia sample #Zr15 and the particle size of the second titania polymeric sol. Unfortunately, the intensity of all the samples is rather low and therefore could not enhance the accurate results of the DLS measurements.

1. de Vos, R. M. in *Inorganic material science* (University of Twente, Enschede, 1998).
2. Maene, N., Nair, B. N., D'Hooghe, P., Nakao, S. I. & Keizer, K. Silica-polymers for processing gas separation membranes: High temperature growth of fractal structure. *Journal of Sol-Gel Science and Technology* **12**, 117-134 (1998).



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

Proposal number:	KW1-05-037		
Experiment title:	Conformation of cyclic polystyrene in entangled state: characterization of single chain in theta solvent and melt state		
Dates of experiment:	21.09. – 23.09.2005	Date of report:	27.03.2006
Experimental team: Names	Addresses		
Michael Kapnistos Dimitris Vlassopoulos Wim Pyckhout-Hintzen	Forth, Crete Forth, Crete FZJ		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

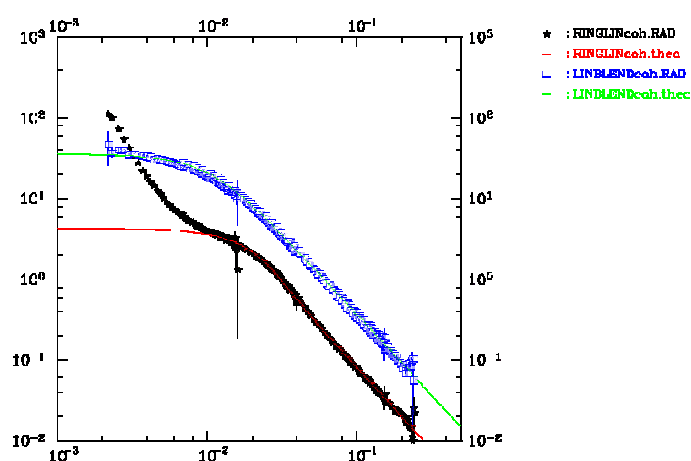


Fig: comparison of the main 'actors' in the melt state

The conformation of ring polymers has been theoretically and experimentally investigated in the past but several problems with samples, sample quality with respect to the ring architecture and others had been reported. In this experiment we use a well characterized ring which had been synthesized by Jacques Roovers and which had been analysed by several techniques before. We were interested also in the blending of

this particular ring with a linear chains. Chains of this particular architecture exhibit new interesting properties which are related to the architectural build-up of the components. To sustain the mixing rheology of ring PS with linear the conformation of the ring polystyrene was measured in both theta and melt state.

The ring polymer in solvent exhibited the expected structural details which were tested against several approaches now available for the ring-type architecture. These approaches are semi-empirical in nature but are valuable as simple exponents which relate again to the intrinsic viscosity of the ring solutions are parameters. The chain conformation data: (see Bensafi et al. Polymer International, 49:175-183(2000)) are described by $R_g \sim N^{1/2}$ and $\nu \sim 0.6$ in good solvent for both linear and cyclic polymer. For theta conditions all values between 0.4 and 0.45 are possible according to this publication. In linear chains the exponent increases even to 0.5. Within the assumption of Gaussian statistics this leads to the expression for every internal distance as: $\langle r_{ij}^2 \rangle = l^2 |i-j| (1 - |i-j|/N)$ which leads to $R_g^2 = Nl^2/12$ for rings in melt.

This changes by excluded volume interactions in different ways. As an assumption: $R_g^2(\text{good solvent limit}) = R_g^2(\text{theta}) \alpha^3$ and α being the Flory swelling. 3 models have been proposed in literature which is very fast summarized as

1. Bloomfield-Zimm
 $\langle r_n^2 \rangle = l^2 n^{1+e} (N-n)^{1+e} / (n^{1+e} + (N-n)^{1+e})$
2. Yu-Fujita
 $\langle r_n^2 \rangle = l^2 n^{1+e} [1 - (n/N)^{1+e}]$
3. Maschke (empirical)
 $\langle r_n^2 \rangle = l^2 n^{1+e} [1 - (n/N)]^{1+e}$

For the formfactor in the Gaussian approximation this leads :

$Pc(q) = 2 \int_0^1 dx (1-x) \exp(-q^2 \langle r_n^2 \rangle / 6)$ with
 $x = n/N$ and $Pc(q=0) = 1$.

The new formfactors can be introduced easily by $\mu = q^2 N^{1+e} l^2 / 6$ ($e=0$ for theta, $e \sim 0.1-0.3$ for good solvent) and numerical integration using mathematical library software.

In order to evaluate without restriction the formfactor of the ring in the blend with linear chains, the linear chain itself was characterized in the melt state and parameters determined. For the RPA equation for ring with linear all linear parameters could be fixed therefore. The results is shown in the upper figure: the pure linear blend behaves perfectly and the ring-linear combination scatters similar to the theta-solution in low angles. The upturn at $q < 0.01$ is NOT due to demixing in the melt as also the solutions without linear chains showed the same feature. In the theta solvent the upturn is shown, in the good solvent limit this is only recognizable which tells us that the 'aggregate' of rings is swollen heavily as well and disappears in the beamstop. From absolute intensities its contribution is of the order of 10%. Both plots show the comparison with the linear chain in log-log and kratky representation. The small peak in the 2-moment of the intensity is typical for the ring structure although it is only shallow. At high q the scattering is again gaussianlike. The critical lengthscale at which pollution of the formfactor of the rings appear is sufficiently separated to allow the simple dimension to be analized with high accuracy. These experiments were the base for upcoming deformed structural analysis.

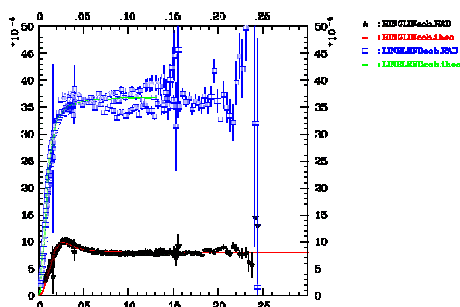
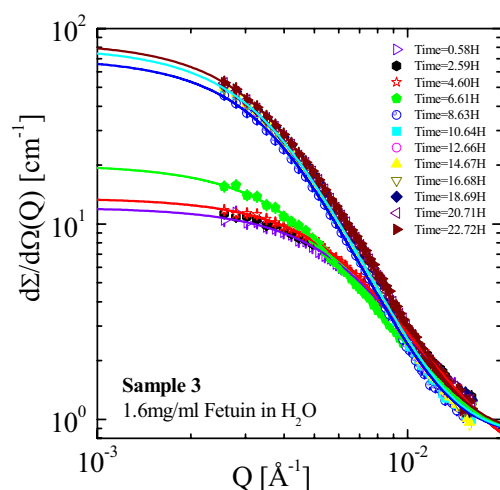


Fig: kratky-representation of ring and ring/lin blend

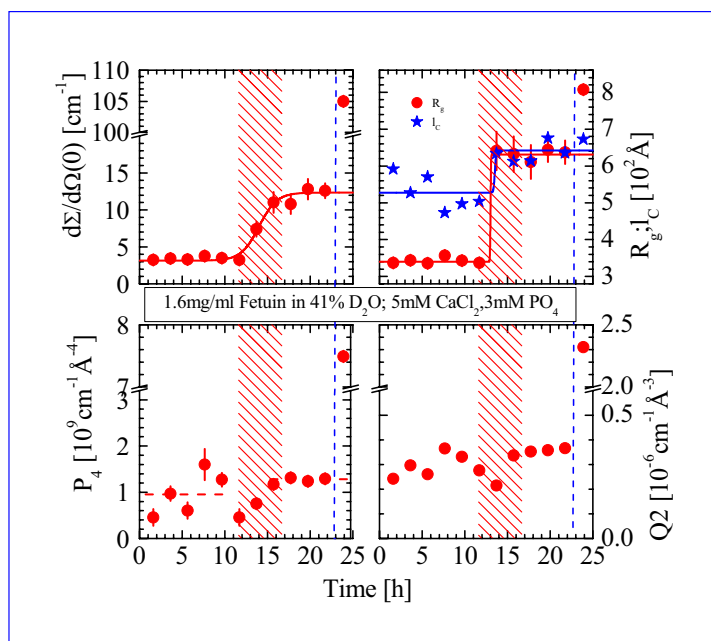
Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-05-039		
Experiment title:	SANS Untersuchung colloidal Protein-Mineral Aggregate bei geringeren Konzentrationen		
Dates of experiment:	16.09. – 19.09.2005	Dates of report:	02.06.2006
Experimental team: Names	Addresses		
Dr. Wolf-Alexander, Heiß	IZKF BioMAT Universitätsklinikum Pauwelsstraße 30 D-52074 Aachen		
Dr. Dietmar Schwahn Dr. Hitoshi Endo	IFF, FZ-Jülich, D-52425 Jülich		
Local Contact:	Dr. Dietmar Schwahn		

Experimental report text body



After having studied the fetuin-A mediated inhibition of calcium phosphate precipitation at a concentration of 2.5 mg/ml fetuin-A, 10 mM CaCl₂, 6 mM PO₄ we decreased the fetuin-A and ion concentrations (1.6 mg/ml bovine fetuin-A, 5 mM CaCl₂, 3 mM PO₄) for this series of experiments. Figure 1 shows the time dependent increase in scattering intensity. Similar to our previous experiments, we observed a two stage ripening. The transformation starts after 5 hours and is finished within eight hours of incubation at room temperature.



jumps up towards the end of this process.

At a 41% D₂O the scattering length density of the protein is matched. Hence only the mineral contributes to the total scattering intensity. The concentrations for this experiment were: 1.6 mg/ml bovine fetuin-A, 5 mM CaCl₂, 3 mM PO₄. During the transition from the first to the second stage we observed again an increase in the scattering intensity and the radius of gyration (from 350 to 560 Å). Simultaneously the surface extension dropped but then slowly increased again. The course of the second moment Q₂ also shows a discontinuous but inverse behavior. Q₂ slowly decreases during transformation but suddenly



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

Proposal number:	KW1-05-041, KW1-05-047, KW1-06-018		
Experiment title:	Chain conformation in novel, natural-synthetic hybrid block copolymers		
Dates of experiment:	26-28/9/05, 11-13/11/05, 24-27/5/06	Date of report:	6 th June 2006
Experimental team: Names	Addresses		
Dr. L.J.R. Foster ^{1,2} Dr. D. Schwahn ² Dr. V. Pippich ²	¹ Bio/polymers Research Group, School of Biotechnology and Biomolecular Sciences, University of New South Wales, Sydney NSW 2052, Australia. ² Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany		 Bio/polymer Research Group
Local Contact:	Dr. D. Schwahn		

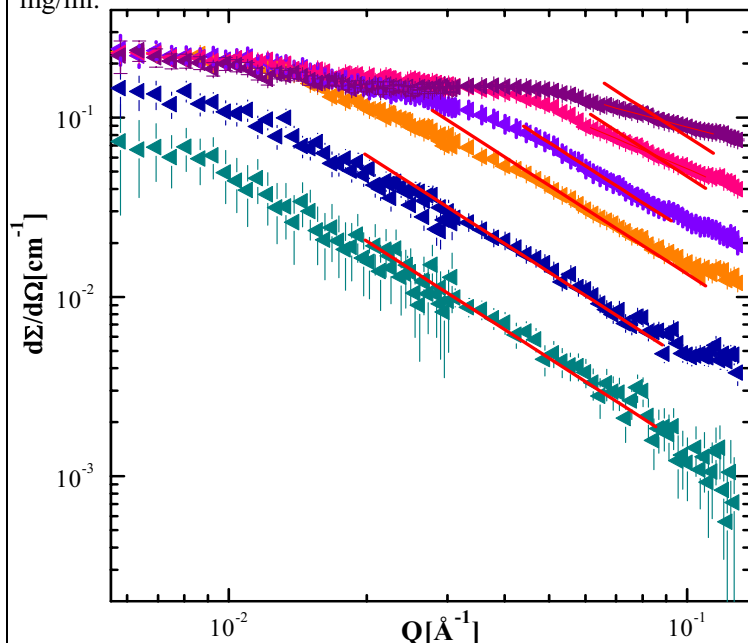
Experimental report text body

Introduction Polyhydroxyalkanoates (PHAs) are a family of biopolyesters synthesized by a wide range of microorganisms. The most common of these biopolymers is Polyhydroxybutyrate (PHB), which has received considerable interest as an environmentally friendly bioplastic and as a biomaterial for biocompatible medical implantation devices. PHB however, is just one member of a family of biopolymers possessing in excess of 105 different monomeric components. These novel biopolymers have material properties ranging from the rigid and highly crystalline to flexible, rather amorphous and elastomeric [1]. Another member of interest is Polyhydroxyoctanoate (PHO). PHB and PHO are representative members of PHAs possessing short and medium chain length substituents in the side chain (*sc*/PHA and *mc*/PHAs).

We have recently synthesised natural-synthetic hybrids of PHB and PHO by ‘end-capping’ hydrophobic PHA chains with hydrophilic diethylene glycol (PHB-DEG and PHO-DEG respectively) [2]. The family of PEGs has a wide range of members varying in molecular mass and structure. A number of biocompatible members have important biomedical functions such as organ and tissue preservation [3]. Material surfaces modified by covalent attachment of PEG chains are resistant to cell and protein adsorption [4]. During solvent casting PHA-PEG hybrids self-assembled into ordered microporous arrays [5]. These microporous films, by virtue of their biocompatible composition and morphology, have the potential to serve a range of biomedical and biotechnological applications.

The objective of this research is to elucidate the influence of the relatively small hydrophilic group in these hybrids on polymer chain conformation, with a particular reference to their ability to form microporous films. In this regard, a synthetic block copolymer: Polystyrene-*b*-polydimethylacrylate which forms highly ordered microporous films is used as a positive control. Thus, based on electron microscopy studies, the degree of organisation in microporous films increases in the following sequence: PS-PDMA > PHB-DEG > PHO-DEG.

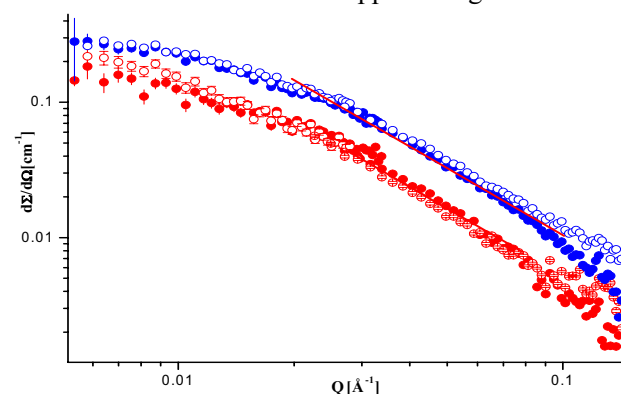
Experimental A series of SANS experiments have been carried out to analyse the conformation of the following polymer chains (a) Polyhydroxyoctanoate (PHO), (b) Polyhydroxybutyrate (PHB), (c) Poly(hydroxybutyrate-co-hydroxyvalerate 8%) (P(HB-co-8HV)), (d) PHO-Diethylene Glycol (PHO-DEG), (e) PHB-Diethylene Glycol (PHB-DEG), (f) Deuterated PHO-hydrogenated DEG (dPHO-DEG) and (g) Polystyrene-*b*-polydimethylacrylate (PS-PDMA). – SANS experiments were performed with biopolymers in solutions using deuterated chloroform and deuterated methylene chloride at a concentration range of 3-100 mg/ml.



Results & Discussion Chloroform is a standard solvent for this family of biopolymers but solvent can play an important role in final device morphology in the processing of these biomaterials [6]. Figure 1 illustrates the change in scattering for PHO in solution with deuterated chloroform at a variety of concentrations. The best visual fit for the slope of the scattering data (1.5 mg/ml) was 1.64, confirming chloroform as a ‘good solvent’. Above about 36 mg/ml the scattering shows the influence of the ‘structure factor’.

Figure 1: Scattering data for solutions of biopolymer PHO in deuterated chloroform with variations in concentration (mg ml⁻¹): (◀) 1.36, (◀) 3.15, (◀) 9.68, (◀) 18.28, (◀) 81, (◀) 72.19.

A Zimm plot of scattering data suggests a PHO chain radius of gyration of approximately 130 ± 5 Å which is maintained until approximately 4 mg ml⁻¹, after which it decreases exponentially, suggesting an overlap concentration between 4 and 9.7 mg ml⁻¹. A linear inverse relationship also exists for the correlation lengths derived from this decrease in apparent R_g.



The patterns of scattering data for the hybridised PHA samples in solution with deuterated solvents were similar to their non-hybridised counterpart (Figure 2). Hybridisation of the PHA chain appeared to have no significant influence on the slope with best estimates at $Q^{-1.64}$. Thus, our preliminary analysis suggests that end-capping the hydrophobic PHA chains with relatively small groups of hydrophilic DEG apparently had no effect on the chain conformation when in solution in chloroform.

Figure 2: Scattering data for solutions of biopolymer PHO and its natural-synthetic hybrid of PHO-DEG in deuterated chloroform with variations in concentration (mg ml⁻¹): (◀) PHO-DEG (4.89) compared to (◀) PHO (3.96) and (◀) PHO-DEG (9.79) compared to (◀) PHO (10.59).

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

Proposal number:	KW1-05-045, KW1-06-008		
Experiment title:	Temperature dependence of conformational and association states in hyperthermophile ICDH		
Dates of experiment:	23.01. – 26.01.2006 20.03. – 22.03.2006	Date of report:	12.06.2006
Experimental team: Names	Addresses		
Marion Jasnin Dominique Madern	IBS 41 rue Jules Horowitz 38027 Grenoble Cedex 01 France		
Joseph Zaccai	ILL 6 rue Jules Horowitz, BP 156 38042 Grenoble Cedex 9 France		
Local Contact:	Martine Heinrich		

Experimental report text body

Isocitrate dehydrogenases (ICDH) are a broadly distributed group of metal-dependent decarboxylating enzymes, involved in cellular energy metabolism. Relations between structure and function of the ICDH and phylogenetic studies have established that this enzyme family is split into three main groups [1]. Group I contains Archaeal and Bacterial NAD(P)⁺-dependent ICDH. Group II is made up of Eukaryotic NAD⁺-dependent ICDH. Group III, which has been identified recently, is made up of Archaeal and Bacterial NAD(P)⁺-dependent enzymes, whose sequences group together at a long evolutionary distance from both groups I and II.

Crystallographic and solution studies have demonstrated that ICDH from groups I and II are dimeric [1-3]. In our laboratories in Norway and France, we are studying the ICDH (III) from the hyperthermophile bacterium *Thermotoga maritima* (Tm), which lives at 80°C, with the aim of achieving a molecular understanding of the group III enzymes. Using analytical centrifugation (AUC) we explored the oligomeric state of Tm ICDH (III) at 20°C, in parallel with enzymes from groups I and II. Compared to all ICDH described to date that are dimeric, Tm ICDH (III) exists also as a tetramer. Experimental sedimentation profiles were well fitted by a mixture of tetramer and dimer.

Recently, crystallisation trials for the ICDH (III) dimer have been successful. X-ray diffraction data have been collected and the structure of the dimer was published few weeks ago (Karlstrom et al., paper in press). In parallel, solutions of the ICDH (III) dimer and of the ICDH (III) tetramer have been successfully prepared, allowing small angle neutron scattering measurements on each of these oligomeric species.

One sample of the ICDH (III) dimer, in 50mM Tris-HCl pH8 containing 0.1M NaCl, and another of the tetramer in the same conditions (for which both oligomeric species exist), were examined on KWS1. Considering the hyperthermophile nature of the enzyme, a significant question relates to the conformational state of Tm ICDH as a function of temperature, and, in particular, to the conformational state of the ICDH enzyme at physiological temperature. Hence, measurements were performed for 2 temperatures, 20°C and 70°C, using the wide range of scattering vectors of KWS1. Three other solvent conditions were also investigated for the dimer (ammonium sulphate, betain and trehalose), in order to see if there was a change in the conformational state of the enzyme due to high hydrophobic interactions. The experiments were performed with a wavelength of 7 Å. Three sample-to-detector distances (2, 4 and 8 m) were employed to cover a Q-range of 0.01-0.2 Å⁻¹. 2-D data were corrected pixel wise for instrumental background and detector efficiency, and radial averaged over the full detector.

Results

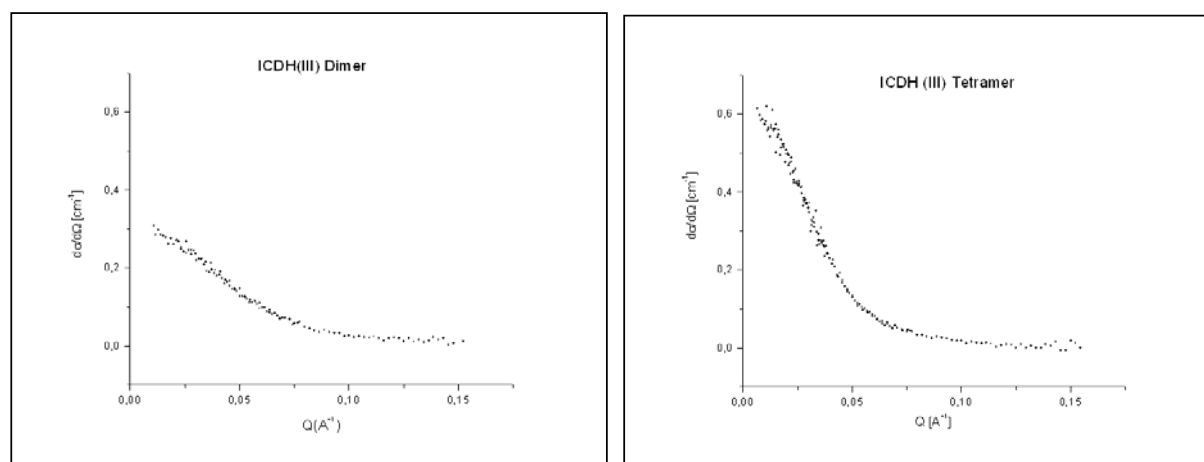


Figure 1. Q-dependence of the scattering cross-sections for the ICDH (III) dimeric (left) and tetrameric (right) states, in 50mM Tris-HCl pH8.

We reported in Figure 1 the Q-dependence of the scattering cross-sections for the Tm ICDH (III) dimer and tetramer, at 20°C. The radius of gyration for both oligomeric species was extracted from the small angle region: 30 Å for the dimer and 45 Å for the tetramer, which is in good agreement with the expected values calculated with the molecular weight.

No change in the conformational state appeared neither at the physiological temperature of the enzyme, nor when the dimeric enzyme was investigated in the other solvent conditions.

Currently, we are using the Svergun's suite of programs and the large angle scattering curves to model the tetramer conformation in terms of the dimer crystal structure.

From the large angle scattering curve of the tetramer, we obtained an average low resolution model for the tetrameric state. This experimental model is compared with the model calculated from both the dimer crystal structure and the large angle scattering curve of the tetramer.

References

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- [3] Karlstrom M, Stokke R, Steen IH, Birkeland NK, Ladenstein R. (2005) Isocitrate dehydrogenase from the hyperthermophile Aeropyrum pernix: X-ray structure analysis of a ternary enzyme-substrate complex and thermal stability. *J Mol Biol.* 45(3):559-77.



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

Proposal number:	KW1-05-046		
Experiment title:	Quaternary structure of a protein-RNA complex involved in nuclear export		
Dates of experiment:	11/12/2005-15/12/2005	Date of report:	20/03/2006
Experimental team: Names	Addresses		
Frank Gabel	European Molecular Biology Laboratory Meyerhofstrasse 1 D – 69117 Heidelberg Germany		
Local Contact:	Vitaliy Pipich		

Experimental report text body

Introduction:

In the experiment conducted at FRJ2 at the FZJ in December 2005, we proposed to record SANS data from a protein-RNA complex named “TAP-CTE” that is involved in the export of viral RNA from the cell nucleus to the cytoplasm [1]. Combined with SANS data of its individual components (isolated TAP and isolated CTE) and with NMR data, we are able to propose a low resolution model of the complex in solution (see Fig. 4 below).

The following samples were measured by SANS experiments on KWS1 at the C2D2 and the C4D4 detector-collimator configurations: Isolated CTE (in 100%H₂O at a concentration of 5 mg/ml), isolated TAP (100% H₂O, 10 mg/ml), TAP-CTE (0%, 42%, 70% and 100% D₂O at 10 mg/ml). All samples were screened for aggregation at the C8D8 configuration. The normalized data sets (against plexiglas) were subtracted for the background scattering determined by the respective buffer runs using the raw data program PRIMUS [2]. The thus processed data sets were then evaluated further using the programs GNOM [3] and DAMMIN [4] in order to determine low-resolution envelopes of the components and the complex as a whole.

Results:

Figure 1 shows the logarithm of the normalized and buffer-subtracted scattering intensities of TAP-CTE at 100% H₂O (in red) and TAP-CTE at 42 % D₂O (in blue) as a function of the scattering vector s (in inverse nm). Figure 2 represents the low resolution model of the CTE (in red), obtained at the matching point of the protein (42% D₂O) with DAMMIN. Superposed is a computer-generated atomic model in blue, based on the CTE base-pair sequence and homology models. The agreement is very good. The experimentally determined molecular weight of 21 kDa is in good agreement with the theoretically predicted one of 20 kDa. The radius of gyration of 23 Angstrom is also very reasonable.

Figure 3 shows a low-resolution model of the whole complex obtained at 100% H₂O with DAMMIN from the experimental data. Its radius of gyration of 27 Angstrom and the molecular weight of 48 kDa (theoretical 50 kDa) are reasonable. Unfortunately, the experimental data at the protein matching point (70% D₂O) did not provide a convincing low-resolution shape of TAP inside the complex, the radius of gyration and molecular weight being too large. A possible explanation may be the high D₂O content in the buffer that is known to favor aggregation.

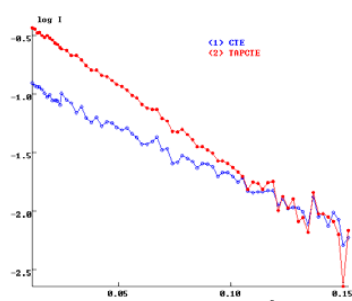


Figure 1

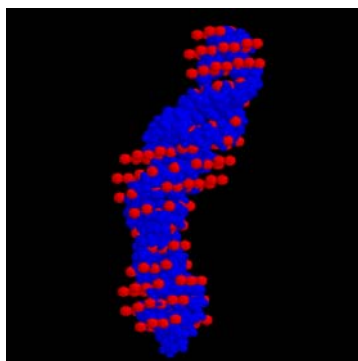


Figure 2



Figure 3

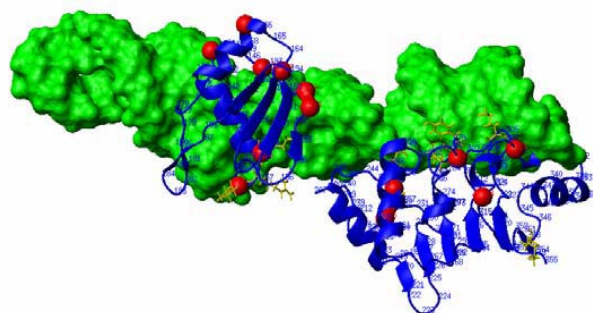


Figure 4

Figure 4 shows a model of the TAP-CTE complex based on the CTE model and the TAP crystal structure [1], optimized against the SANS data. In this model, NMR chemical shift perturbations, residual dipolar couplings and mutational data were equally taken into account. At the moment, we are optimizing the information provided by NMR.

References:

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

Proposal number:	KW1-05-047, KW1-05-063, KW1-06-011, KW1-06-018		
Experiment title:	Chain conformation in novel, natural-synthetic hybrid block copolymers		
Dates of experiment:	11-13/11/05, 26-28/1/06, 15-16/4/06, 24-27/5/06	Date of report:	6 th June 2006
Experimental team: Names	Addresses		
Dr. L.J.R. Foster ^{1,2} Dr. D. Schwahn ² Dr. V. Pippich ²	¹ Bio/polymers Research Group, School of Biotechnology and Biomolecular Sciences, University of New South Wales, Sydney NSW 2052, Australia. ² Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 524425 Jülich, Germany		 Bio/polymer Research Group
Local Contact:	Dr. D. Schwahn		

Experimental report text body

Introduction Polyhydroxyalkanoates (PHAs) are a family of biopolyesters synthesized by a wide range of microorganisms. The most common of these biopolymers is Polyhydroxybutyrate (PHB), which has received considerable interest as an environmentally friendly bioplastic and as a biomaterial for biocompatible medical implantation devices. PHB however, is just one member of a family of biopolymers possessing in excess of 105 different monomeric components. These novel biopolymers have material properties ranging from the rigid and highly crystalline to flexible, rather amorphous and elastomeric [1]. Another member of interest is Polyhydroxyoctanoate (PHO). PHB and PHO are representative members of PHAs possessing short and medium chain length substituents in the side chain (*sc*/PHA and *mc*/PHAs).

We have recently synthesised natural-synthetic hybrids of PHB and PHO by 'end-capping' hydrophobic PHA chains with hydrophilic diethylene glycol (PHB-DEG and PHO-DEG respectively) [2]. The family of PEGs has a wide range of members varying in molecular mass and structure. A number of biocompatible members have important biomedical functions such as organ and tissue preservation [3]. Material surfaces modified by covalent attachment of PEG chains are resistant to cell and protein adsorption [4]. During solvent casting PHA-PEG hybrids self-assembled into ordered microporous arrays [5]. These microporous films, by virtue of their biocompatible composition and morphology, have the potential to serve a range of biomedical and biotechnological applications.

The objective of this research is to elucidate the influence of the relatively small hydrophilic group in these hybrids on polymer chain conformation, with a particular reference to their ability to form microporous films. In this regard, a synthetic block copolymer: Polystyrene-*b*-polydimethylacrylate which forms highly ordered microporous films is used as a positive control. Thus, based on electron microscopy studies, the degree of organisation in microporous films increases in the following sequence: PS-PDMA > PHB-DEG > PHO-DEG.

Experimental We have applied SANS to investigate the conformation of polymer chains in solution with the purpose of investigating their ability, or lack thereof to self-assemble into microporous films. Complementing our studies of these polymers in solution we have also applied SANS to their melt-pressed and solution cast films. In the former we have also investigated the affects of temperature through the melt-phase (25-80°C).

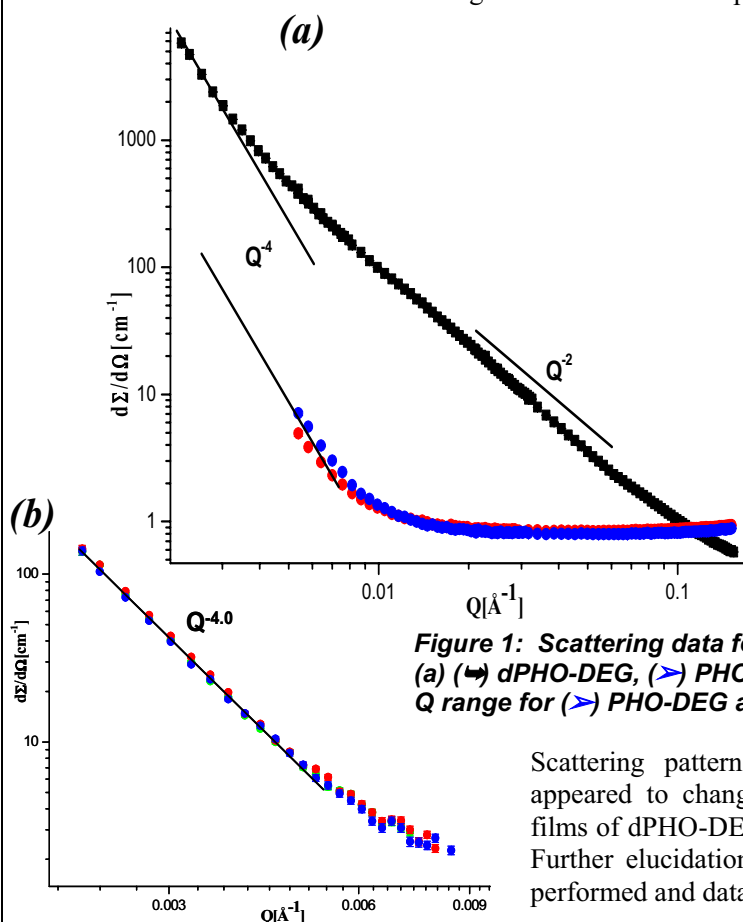


Figure 1: Scattering data for melt-pressed films at room temperature (a) (■) dPHO-DEG, (▲) PHO-DEG and (▲) PHO. (b) enlargement of Low Q range for (▲) PHO-DEG and (▲) PHO.

Results & Discussion SANS analysis of melt-pressed films of PHO, PHO-DEG and dPHO-DEG were performed to determine incoherent background scattering and to investigate the possibility of any local organisation. Figure 1b reveals the scattering at low Q (Q^{-4}) which maybe associated with the chain organisation during processing such as lamellae. In contrast, the scattering pattern for dPHO-DEG, which consists of 80% deuterated PHO end-capped with protonated DEG, changed from Q^{-2} (Gaussian coils) at high Q to Q^{-4} in the low Q range. We can theorise that during the melt preparation process the DEG segments orientate themselves to form non-ordered thin 'platelet-like' structures (Figure 1).

Scattering patterns of PHO films generated during melting appeared to change little, however changes were apparent for films of dPHO-DEG over its melting point between 50 and 60°C. Further elucidation using a blend of PHO and dPHO has been performed and data is currently under analysis.

Our results are consistent with the work of Beaucage and films of PHB which also showed a power law of -2 [6]. Across the Q range examined, rather than a discrete transition regime between power law -2 and power law -4 scaling, the polymer displayed a gradual transition.

Thus, our results suggest end-capping of the hydrophobic PHA chains with a small synthetic hydrophilic group has an influence on polymer chain conformation during melt and solvent processing of the polymer into bioplastic films.

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- [2] Sanguanchaipaiwong, V; Gabelish, CL; Hook, J; Scholz, C. & Foster LJR. *Biomacromolecules* **2004**;5(2):643.
- [3] Harris JM. *Poly(ethylene glycol) chemistry: biotechnical and biomedical applications*. New York, USA: Plenum **1992**.
- [4] Inada Y, Matsushima A, Kodera Y, Nishimura H. *J. Bioact Compat Polym.* **1990**;5:343.
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Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW1-05-048		
Experiment title:	SANS investigations of the amorphous layer on aragonite nacre platelets		
Dates of experiment:	31.10. – 03.11.2005	Date of report:	21.06.2006
Experimental team: Names	Addresses		
Helmut Cölfen	Max-Planck-Institute of Colloids and Interfaces Colloid Chemistry Am Mühlberg 1 14476 Golm Germany		
Vitaliy Pipich Dietmar Schwahn	Institut für Festkörperforschung Forschungszentrum Jülich D-52425 Jülich / Germany		
Local Contact:	Vitaliy Pipich		

Experimental report text body

The aim of the present research was to understand the internal structure of aragonite plates extracted from nacre of the seashell *Haliotis Laevigata*. By HRTEM and solid state ^1H & ^{13}C -NMR, an amorphous layer of the calcium carbonate was observed. By SANS we measured a cleaned powder of the nacre in $\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures of different D_2O -content and in air.

The scattering from the proteins inside the mineral is almost contrast-independent; the volume fraction, volume and mineral/protein contrast are constant. The radius and volume fraction of the bound proteins are 53Å and near 6%, respectively. The latter value is in agreement with 5% protein content from thermogravimetry. Blue and green lines are the preventative fitting curves of data by the Guinier law to highlight the bimodal distribution in system.

In Figure 2 the first ($Qd\Sigma/d\Omega(Q)$) and second ($Q^2d\Sigma/d\Omega(Q)$) moments of the scattering curve from Figure 1 are depicted showing clearly a bimodal distribution. The area under second moment is proportional to the volume fraction Φ and the scattering contrast $\Delta\rho^2$: $Q_2 = \int_0^\infty Q^2 d\Sigma/d\Omega(Q) dQ = 2\pi^2\Phi(1-\Phi)\Delta\rho^2$. The red lines represent a Gaussian fit of the first and second moment of the scattering within the intermediate Q-range (II); the green lines represent a lognormal distribution of the "bound" proteins. The ratio between first and second moment gives a chord-size $l_c = \pi Q_1/Q_2$.

In conclusion, we might have observed scattering from an amorphous layer of the aragonite calcium carbonate surface. From the ratio between first and second moment a dimension of the amorphous discs was calculated near 700Å.

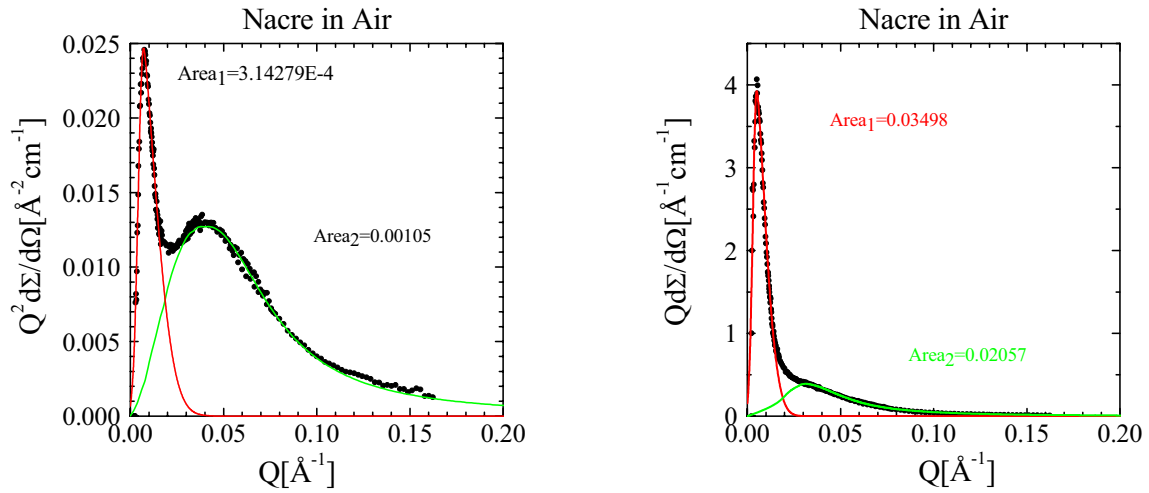


Figure 2. The second and first moment of the scattering curve of the nacre powder in Fig. 1.



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

Proposal number:	KW1-05-049		
Experiment title:	New Zirconium based catalysts for living olefin polymerization		
Dates of experiment:	2005-11-03	Date of report:	2006-06-05
Experimental team: Names	Addresses		
Aizhen Niu Jörg Stellbrink Jürgen Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

Coates et al. [1] reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. However, the kinetics and mechanism of living olefin polymerization is still poorly understood. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization.

In recent SANS experiments we investigated the living polymerisation of poly(hexadienes) using a Titanium catalyst/MAO activator. We found that this system shows some unexpected precipitation after mixing of the individual compounds at low temperatures. I.e. rigorous stirring is required for keeping the catalyst/co-catalyst complex in solution, which is a prerequisite for successful polymerisation. Unfortunately this is not possible in the SANS cell and in particular not in the NMR cell, so that an absolute calibration in terms of sample concentration was not achievable.

Therefore we used another catalyst system to avoid this solubility problem. The new catalyst system contains a Hafnium complex as catalyst and low molecular weight Boron hydride compounds as activator. In this experiment, catalyst, cocatalyst and monomer mixture was stored at -80°C after sealed off in chemistry lab. Then it was warm up to 20°C for the in-situ SANS measurement. Figure 1 shows that the polymerization is very fast at the beginning of the polymerization and the whole conversion of the monomer is only 40% after the polymerization finished.

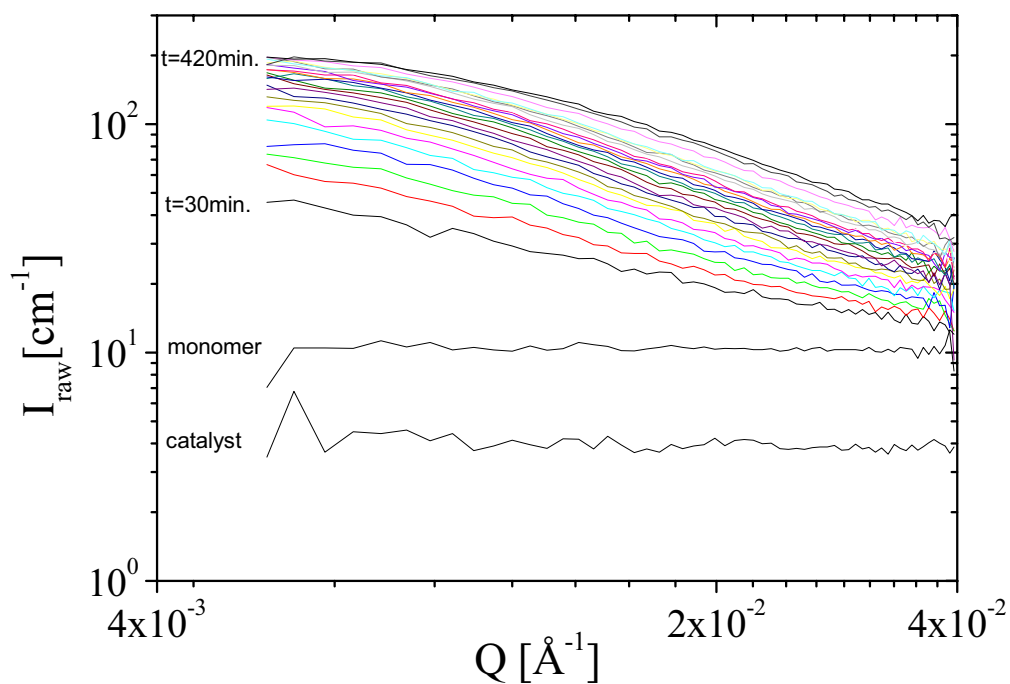


Figure 1: Metallocene catalysed Polymerisation of octene followed by real time SANS experiments at 20°C .

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

Proposal number:	KW1-05-050		
Experiment title:	Highly turbid, highly efficient microemulsions with sticker polymers		
Dates of experiment:	28.10.2005	Date of report:	21.03.2006
Experimental team: Names	Addresses		
Henrich Frielinghaus, Christian Frank, Simona Maccarrone, Martin Brodeck, Gaetano Mangiapia	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich 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

The initial inspection of microemulsions is done by phase diagram measurements. Usually the visual inspection of the turbidity and of birefringence allows the identification of basically all known phases. Especially the one-phase bicontinuous microemulsion is easily to determine in the neighborhood of two-phase regions. If the surfactant becomes more and more efficient – this can also be obtained by the addition of polymers – the bicontinuous microemulsion scatters light very strongly, and the strongly scattering one-phase state cannot be distinguished anymore from the two-phase state. The idea of this measurement was determination of the minimal surfactant content for efficiency boosted microemulsions by small angle neutron scattering (SANS). The efficiency of the non-ionic $C_{10}E_4$ surfactant was increased by a $C_{10}E_{100}$ sticker polymer with amounts of more than 10% relative to the total amphiphile. Sticker polymers with a short hydrophobic sticker and a normally long hydrophilic block have been approved to boost the efficiency of surfactants equally well compared with amphiphilic diblock copolymers. The initial idea of the SANS experiments was the direct observation of the Porod scattering of the demixing domains. The actual results gave us an indirect conclusion for some of the samples.

Two example measurements are shown in figure 1. At the lower temperature a for bicontinuous microemulsions typical correlation peak is observed at $Q = 0.005\text{\AA}^{-1}$. This is not the case for the higher temperature. Since the temperature is the only change between the measurements, the sample formed a bicontinuous microemulsion at the lower temperature, and the sample was demixed at the higher temperature for the following reason: The amount of surfactant does not change and, therefore, allows to form domains of only one length scale. This length scale has been observed at the lower temperature.

The initially expected Porod behavior at lower scattering angles ($Q < 0.005\text{\AA}^{-1}$) was not observed at the higher temperature since the Q -range was limited. This Porod behaviour of the macro-domains is to be distinguished from the Porod scattering of the micro-domains. The presence of surfactant always allows to form micro-

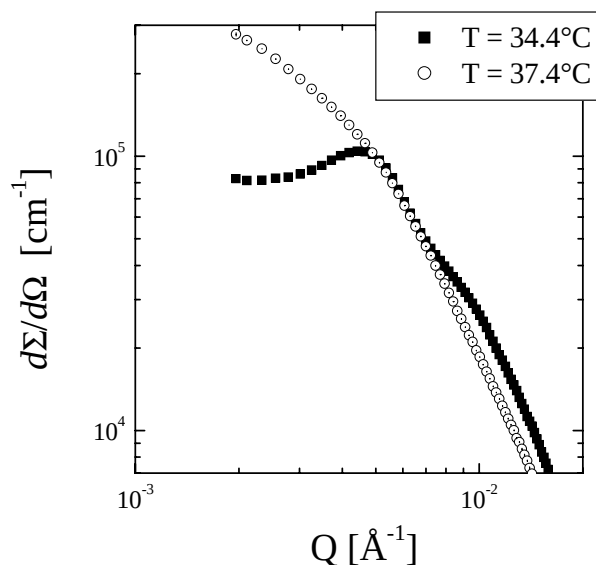


Figure 1: Macroscopic cross section as a function of the scattering vector Q of a turbid microemulsion at two different temperatures. At the lower temperature a correlation peak is found, which indicates a one-phase microemulsion. At the higher temperature the correlation peak is lost, and the microemulsion forms two phases. It should be mentioned that the transmission is 7%, and multiple scattering is an issue. For instance the shoulder at $Q = 0.01 \text{ \AA}^{-1}$ (34.4°C) is due to multiple scattering.

domains within macro-domains with enough surfactant. An extension to lower Q values was tried by the reduction of the wavelength to $9 \text{ \AA}$ and $11 \text{ \AA}$ for the lower temperature. Unfortunately, the correlation peak was strongly diminished due to the multiple scattering, and the whole measurement did not contain any useful information anymore. Already the in figure 1 presented measurements contain multiple scattering effects. The transmission was 7%, and a clear shoulder at $Q = 0.01 \text{ \AA}^{-1}$ was observed. Since no lamellar phase is expected, the double scattering of the correlation peak is the right explanation for the shoulder.

The remaining samples contained even less surfactant and therefore a correlation peak at even lower Q was expected. Due to multiple scattering at these even larger structures (the transmission was 2%) the correlation peak was not observable. Only a Porod behavior from the micro-domains was observed. At the higher temperature a similar scattering pattern as in figure 1 was obtained. For these other samples the indications of the bicontinuous microemulsion state and the two phase state are weaker as for the first sample. In a repetition of this experiment a much thinner sample (0.1 mm) or a much lower contrast ($\text{D}_2\text{O}/\text{H}_2\text{O}$ mixtures) would be desired in order to avoid multiple scattering and to allow measurements at even lower Q with longer wavelengths. At present we did not follow this suggestion since the extremely high polymer contents were not essential for the actual research. Nonetheless, the obtained technical knowledge will be used for applications in the future where polymers will allow an extremely high efficiency boosting. Then visual inspections will not yield the desired results, and only neutron scattering experiments with the right contrast or sample thickness can distinguish the different phases.



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

Proposal number:	KW1-05-051		
Experiment title:	SANS investigation on the origin of the dynamic heterogeneity in poly(vinyl acetate).		
Dates of experiment:	10-01-2006 to 13-01-2006	Date of report:	05-06-2006
Experimental team: Names	Addresses		
1. Madhusudan Tyagi 2. Angel Alegria	Donostia International Physics Center, 20018, San Sebastián, SPAIN Física de Materiales, Facultad de química, Apdo. 1072, 20080 San Sebastián, SPAIN		
Local Contact:	M. Heinrich		

Experimental report text body

Poly(vinyl acetate) (PVAc) is a well known amorphous polymer which presents a series of curious experimental peculiarities¹. We recently studied² PVAc using quasi-elastic neutron scattering (QENS), dielectric relaxation spectroscopy (DRS) and ¹³C NMR. The characteristic times observed by QENS showed an anomalous dependence of momentum transfer, indicating the possible existence of heterogeneities in the system even at high temperatures. In addition, spin lattice relaxation times T_1 were found to be decoupled from dielectric characteristic times. Interestingly, all the carbon atoms (including in methyl group and carbonyl group) showed same temperature dependence of T_1 times indicating homogeneity at monomer level. Based on these results it was concluded that the dynamics of PVAc shows anomalous behaviour because of the heterogeneous dynamics even far above glass transition temperature. In order to go deeper into the problem recently, we made measurements on small molecule analog of poly(vinyl acetate) (trimer of vinyl acetate) using neutron spin echo³, DRS and ¹³C NMR. The decoupling of characteristic times between DRS and ¹³C spin-lattice relaxation time reduced greatly because one does not expect heterogeneities to be present at high temperatures in small molecule glass formers. The purpose of this experiment was to look for any signs of corresponding structural heterogeneities in PVAc by measuring the static structure factor $S(Q)$ and form factor $P(Q)$ of PVAc in low-Q range. The static structure factor of PVAc was measured at three different temperatures viz. 336K, 377K and 413K. The form factor of PVAc in 90dPVAc/10hPVAc blend was also measured at the same temperatures. For this purpose, the detector positions were set at three distances, namely 2m, 8m and 20m to cover the Q range roughly between 0.003 and 0.16 Å⁻¹. In addition, measurements were made with empty beam, with plexi glass and boron carbide for background and sensitivity of the detectors.

The corrected experimental data is shown in Figs.1 and 2. The abnormality in the data can be seen from the presence of so-called porod regime at low Q -values which might be a consequence of some air bubbles of micrometer size in the samples. Nevertheless, the actual data for the samples could be separated as porod regime has a well defined set of characteristics. The refined data does not show a clear peak in the structure factor (open symbols Fig.1). However, it shows a continuous increase in the low- Q regime which might be an indication of domains whose sizes are bigger than the spatial scales explored by SANS. However, the presence of porod regime makes it difficult to conclude anything conclusive from these measurements. On the other hand, the form factor of PVAc could be fitted to modified Debye form:

$$P(Q) = \frac{2}{(U+1)x^2} \left[(1+Ux)^{-1/U} - 1 + x \right]$$

where $U=(M_w/M_n)-1$ and $x=\langle R^2 \rangle Q^2 / 1+2U$; when modified to polydispersity ($M_w/M_n=2.5$) of the sample. The resulting radius of gyration R_g changes from 91 to 96Å between the measured temperatures 336K and 413.

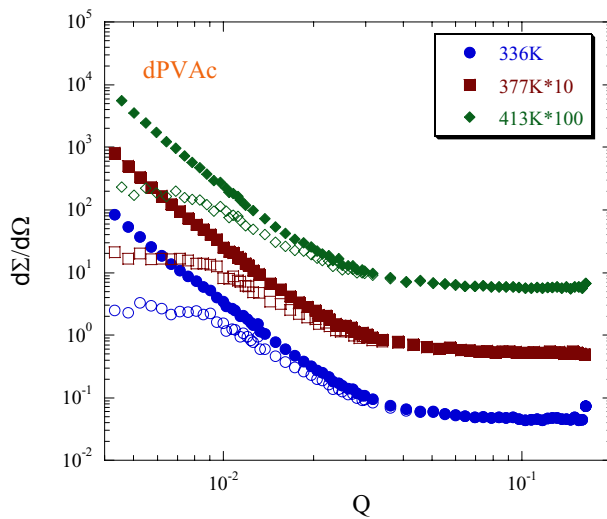


Fig.1: The scattering cross sections for dPVAc at measured temperatures. For the sake of clarity, actual data has been multiplied by 10 and 100 in case of 377K and 413K, respectively. The corresponding empty symbols show the data after making corrections for porod regime at low- Q values.

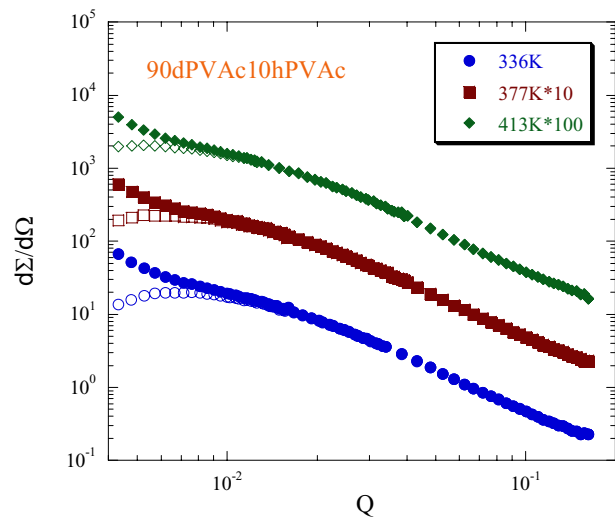


Fig.2: Scattering cross sections for 90dPVAc10hPVAc at different temperatures. For the sake of clarity, actual data has been multiplied by 10 and 100 in case of 377K and 413K, respectively. The corresponding empty symbols show the data after making corrections for porod regime at low- Q values.

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2. M. Tyagi, A. Alegria and J. Colmenero, *Journal of Chemical Physics*, Vol. 122, 244909 (2005).
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Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-05-052		
Experiment title:	Aggregation behaviour of disk-shaped porphyrin catalysts		
Dates of experiment:	21-22 Jan. 2006	Date of report:	22-May-2006
Experimental team: Names	Addresses		
Van Hameren, Richard Feiters, Martin Elemans, Hans Rowan, Alan Nolte, Roeland	Institute for Molecules and Materials Radboud Universiteit Nijmegen Toernooiveld 1 6525 ED Nijmegen The Netherlands		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

In Nature, porphyrins are abundantly applied, both as catalysts and chromophores. For example, manganese porphyrins are known to be able to catalyse epoxidation reactions. In this type of reactions, an oxygen atom is incorporated into the double bond of an alkene, yielding an epoxide (Figure 1)¹.

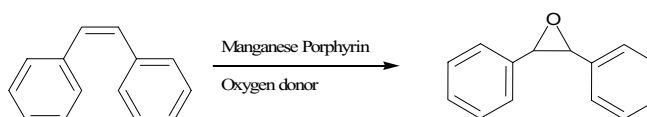


Figure 1. Schematic representation of the epoxidation of *cis*-stilbene, catalysed by **1**.

Recently, we have synthesised manganese porphyrin trimer **1** (Figure 2). In CD₂Cl₂ solution this molecule is expected to self-assemble in small columnar stacks². Catalysis experiments involving the epoxidation of *cis*-stilbene by **1** have demonstrated that the addition of bidentate axial ligands, such as pyrazine and DABCO, to this catalyst during the reaction, changes the turnover frequency compared to the situation when they are absent. Surprisingly, we found that when the amount of DABCO or pyrazine was increased (0 → 3 eq. vs. **1**), an initial decrease in turnover number and an optimum at 2.5 equivalents of axial ligand were observed. We attribute this behaviour to a complicated interplay between the activation and related to that the reactivity of the catalyst, as well as changes in the stacking behaviour of the catalyst molecules. From literature it is known that the presence of nitrogen-based ligands can increase the catalytic reactivity,^{1,3} and in addition, it is expected that upon their binding to the catalyst the stacking of **1** is either disfavoured or enhanced.

By means of SANS, we have investigated the stacking behaviour of **1** in CD₂Cl₂ as a function of the amount of axial ligand present (pyrazine or DABCO). In addition, we have investigated the influence of other chemicals used for the catalysis, e.g. mesitylene (internal standard) and *cis*-stilbene (substrate), on the stacking behaviour.

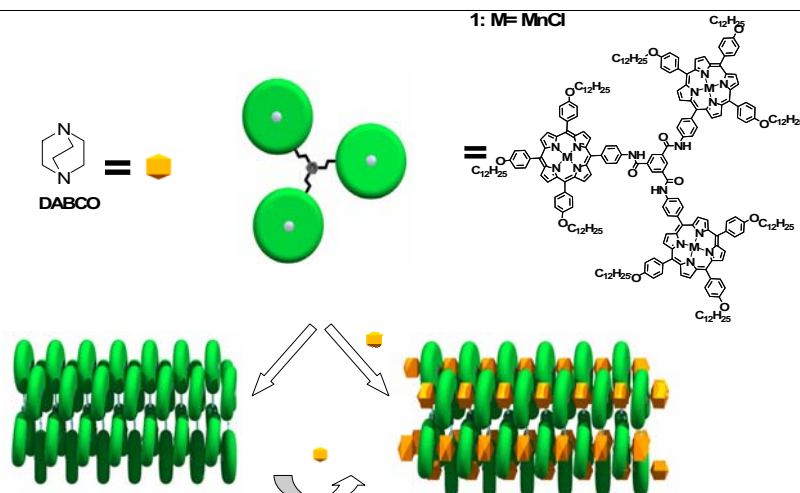


Figure 2. Schematic representation of the formation of a supramolecular polymer stacks by **1** and the binding of DABCO within these stacks.

The SANS measurements unambiguously demonstrated the presence of cylindrical particles in a solution of pure **1** in CD_2Cl_2 ($[\mathbf{1}] = 6.6\mu\text{M}$), with a diameter of 2.3 nm, which is in excellent agreement with the diameter of the aromatic part of the molecule. The average length of the cylinders was 7.1 ± 0.1 nm, corresponding to approximately 14 molecules of **1**, assuming a distance between two molecules of 0.5 nm (molecular mechanics modelling, force field: MMFF94). Upon gradual addition of either pyrazine or DABCO to the solution, the diameter of the cylinder remains constant within experimental error, while the average length of the stack decreases (Figures 3A&B). Apparently, the binding of axial ligands competes with the stacking process, resulting in the formation of smaller stacks of **1**. The effect is somewhat more pronounced for the DABCO ligands, which might be related to a slightly smaller N-N distance in this compound as compared to pyrazine (N-N distance DABCO = 0.256 nm, pyrazine = 0.278 nm (Semi-Empirical calculations, parameters: PM3)).

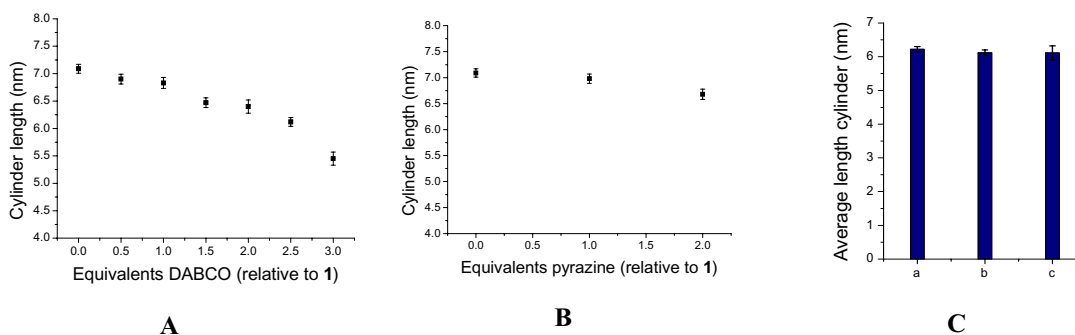


Figure 3. Overview of the SANS-measurements. The average length of the stack decreases with both an increasing amount of DABCO (A) and pyrazine (B) and does neither change in presence of the mesitylene and cis-stilbene nor substitution of CH_2Cl_2 by toluene-D8 (C legend: a = toluene-D8, b = CD_2Cl_2 , c = b + mesitylene + cis-stilbene) ($[\mathbf{1}] = 6.7\mu\text{M}$, 2.5 equivalents of DABCO).

In addition, the SANS measurements demonstrated that neither a change in solvent from CD_2Cl_2 to toluene-D8, nor the presence of chemicals used for catalysis lead to a substantial change in stacking behaviour (Figure 3C).

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

Proposal number:	KW1-05-054		
Experiment title:	The interaction of polypeptides with carbon nanotubes		
Dates of experiment:	07.03.-11.03.2006	Date of report:	05.06.2006
Experimental team: Names	Addresses		
COHEN, Yachin GRANITE, Merav	Department of Chemical Engineering, Technion, Haifa, ISRAEL 32000 Department of Chemical Engineering, Technion, Haifa, ISRAEL 32000		
Local Contact:	Dr. Wim Pyckhout-Hintzen		

Experimental report text body

Background

Carbon nanotubes are known by their remarkable unique mechanical, optical, thermal and electronic properties. In production they tend to form bundles with different diameters and chirality, which results in diminishing of their unique properties. Many efforts have been made in order to separate bundles and form stable dispersions. Significant recent developments have been in the use of synthetic polypeptides ("un-natural proteins") for dispersing single-walled carbon nanotubes (SWCNTs) in water.

Objectives

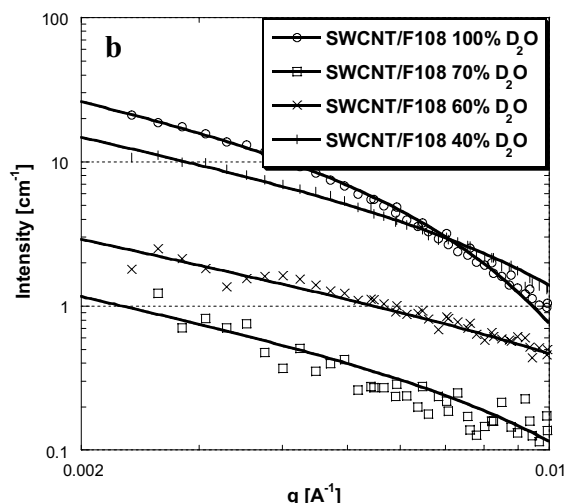
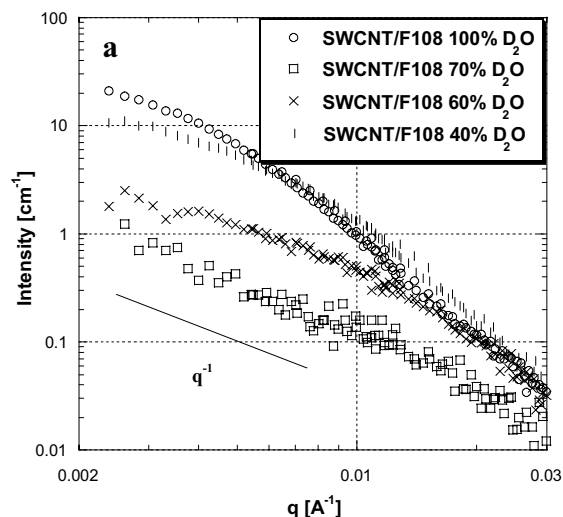
The objective of this study is to understand the way polypeptides and block copolymers interact with the surface of SWCNTs and to elucidate the conformation of the polymer interacting with the nanotubes. Whether it is the "polymer wrapping" model, where the polymer is tightly wrapped about the nanotube surface or a rather loose adsorption so that the polymer coil surrounding the tubes form steric hindrance to re-aggregation.

Experiments

SANS measurements were conducted at KWS1 and due to the elongated feature of the carbon nanotube and the polymers around it the 20m sample-detector distance was required. Measurements of the bare polymer solutions, in different D₂O/H₂O mixtures, were conducted to ascertain the bare polymer conformation and scattering length density, they were followed by SANS measurements of the nanotube dispersions with contrast variation to evaluate the polymer conformation in the adsorbed state. Four polymers were studied: synthetic block copolymer of styrene (~5kDa) and sodium acrylate (~30kDa) (PSSA), a di-block copolymer of ethylene oxide and propylene oxide (Pluronic F-108), a synthetic oligo-peptide: poly (FFDD) [single letter notation: F=phenyl alanine, D = aspartic acid] with about 30 amino-acid units and Lysozyme.

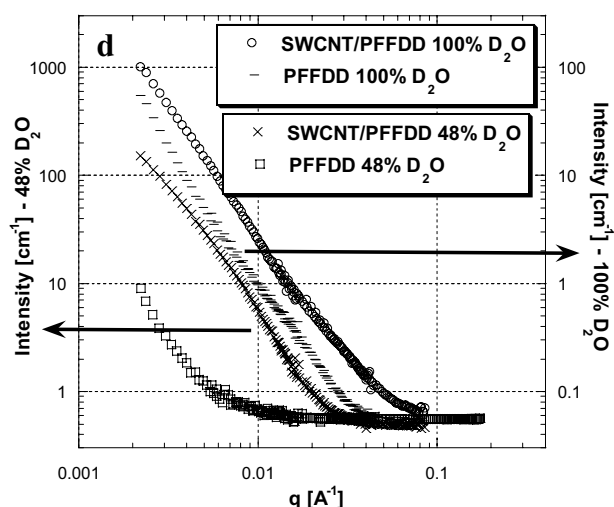
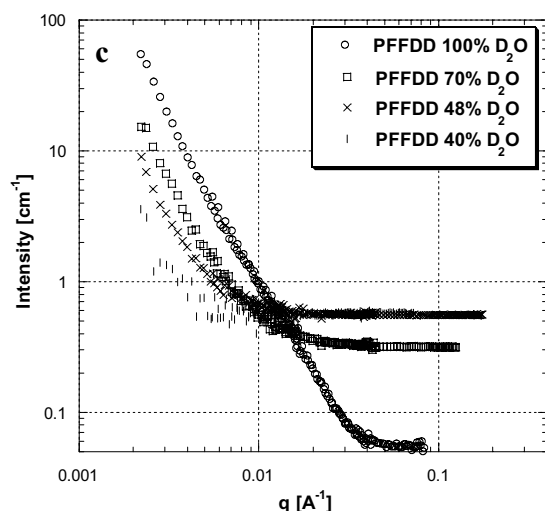
Results

The scattering results of SWCNT/F-108 dispersions containing 0.5% (w/w) SWCNT and 5% Pluronic F-108 in four different D₂O/H₂O mixtures after subtractions are shown in figure (a) below. Figure (b) and the table below show the Guinier approximation for cylinder, $I(q) \sim q^{-1} \exp(-1/2 r_c^2 q^2)$, and the cross-section radius of gyration (r_c) for different contrasts. The SANS pattern of SWCNT/F-108 in 60/40 D₂O/H₂O shows nearly a q^{-1} power law of $I(q)$ as well as the smallest gyration radius, which may indicate a significant tight binding of the hydrophobic blocks to the nanotubes.



Guinier Cylinder Approximation					
% D ₂ O	Gyration radius (r_c)	% D ₂ O	Gyration radius (r_c)	% D ₂ O	Gyration radius (r_c)
100	200	80	205	60	67
90	189	70	120	40	125

The scattering patterns of the polypeptide (FFDD) containing 1% (w/w) in four different D₂O/H₂O mixtures and the results of SWCNT/poly (FFDD) dispersions containing 0.2% (w/w) SWCNT and 1% poly (FFDD) in two different D₂O/H₂O mixtures are both shown below in figures (c) and (d) respectively. It is very clear that the small amount of nanotubes increases the intensity at the low q range and presents an overlapping of intensity patterns at large q range. The bare polymer at 40% D₂O shows almost constant scattering which may indicate an almost matched contrast.





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

Proposal number:	KW1-05-056		
Experiment title:	Microstructure Investigation of Porous Doped Graphites using Small-Angle Neutron Scattering		
Dates of experiment:	07.02.06 to 08.02.06	Date of report:	13.06.2006
Experimental team: Names	Addresses		
K. Mergia, K. Stefanopoulos	National Centre for Scientific Research “Demokritos” 15310 Aghia Paraskevi Attikis Greece		
Local Contact:	Martine Heinrich		

Experimental report text body

The aim of the project was to measure the pore microstructure in samples of doped and undoped graphites using the small-angle neutron scattering (SANS) technique. The samples have a porosity that varies from totally closed to totally open. Closed porosity cannot be determined with the conventional methods and SANS is a powerful tool for determining the size distribution and volume fraction of porosity in nanoporous materials.

Carbon and graphite are attractive materials for high-temperature applications due to their high thermal conductivity, low electrical resistivity, high strength, high modulus, excellent thermal shock resistance and light weight. They are widely used as engineering materials, such as heaters, electrical contacts, high-temperature heat exchangers, rocket nozzles, plasma facing materials in fusion devices and leading edges of aircraft wings, etc. [1–3]. A main drawback of carbon-based materials is their chemical erosion under hydrogen bombardment which for plasma facing applications has to be avoided [4]. Doping of carbon with small amounts of certain elements is known to reduce chemical erosion. In addition, other properties such as high thermal conductivity and high thermal shock resistance can be also improved by doping of carbon. Some dopants show a catalytic degree on the graphitization, leading to a higher degree of graphitization.

For fabricating the doped graphite samples a self-sintering powder of mesophase carbon based on petroleum residues was used. The powder was jet-milled down to a mean particle size of the order of 1 μm . As dopants metallic carbides showing catalytic effect on the graphitization were used i.e. TiC and ZrC. The carbides were added to the carbon powder up to a metal concentration of ~ 4 at% [5]. The graphitization temperature employed was 2700 and 2750°C with a dwell time of 1 hour. After the graphitization process the doped materials were subjected to an additional hot isostatic pressing (HIP) step to obtain a higher densification.

Five samples of undoped and doped graphites were measured at room temperature using Small Angle Neutron Scattering. The existence of dopants influence the type and the extent of the porosity present in the samples during the fabrication process. As dopants TiC and ZrC were used.

The contrast matching technique was used in order to distinguish open from closed porosity using the adequate ratios of H₂O/D₂O. All the samples were measured dry and wet.

In fig. 1 is shown the cross section versus the scattering vector of undoped graphite with 12.3% total porosity and 6.9% open porosity, measured dry (open circles) and wet (open squares). As it is expected the scattering is lower for the wet samples since in this case the scattering from the open pores is matched out with that of the matrix and only the scattering from the closed pores is revealed. In fig. 2 the cross section versus the scattering vector of TiC doped graphite with 10.5 % total porosity and no open porosity, measured dry (open circles) and wet (open squares). In this case the scattering from the wet and dry samples is almost identical as it would be expected since the sample has only closed porosity.

The treatment of the data is underway for the evaluation of the results.

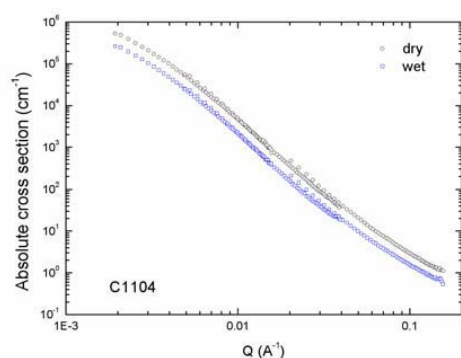


Fig. 1 Absolute cross versus scattering vector of undoped graphite with 12.3% total porosity and 6.9% open porosity, measured dry (open circles) and wet (open squares).

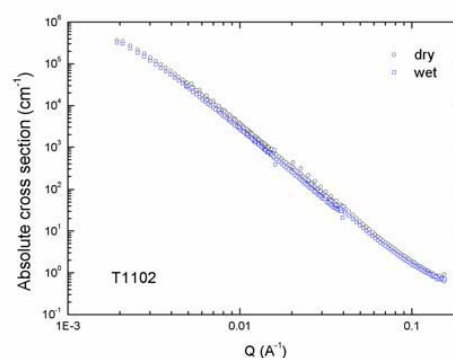


Fig. 2 Absolute cross versus scattering vector of TiC doped graphite with 10.5 % total porosity and no open porosity, measured dry (open circles) and wet (open squares).

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

Proposal number:	KW1-05-057		
Experiment title:	Neutron scattering study of IKK kinase complex		
Dates of experiment:	December 10 – 15, 2005	Date of report:	20.02.2006
Experimental team: Names	Addresses		
Xavier Lee¹, Joseph DiDonato¹ Guiseppe Zaccai²	1 Department of Cancer Biology, Cleveland Clinic Foundation, 9500 Euclid Avenue, Cleveland, Oh USA 44195 2 Institut de Laue-Langevin, Avenue de Martyrs, 38042, Grenoble, France		
Local Contact:	Dr. Dietmar Schwahn		

Experimental report text body

Results

IKK kinase complex is an important unity in signal transfer in living cells. IKK complex is consisted of three components, for IKK α , IKK β and IKK γ . During the experiment in Juelich we tried to study the three components separately. Based on the results we obtained in July 2005 at ILL, Grenoble, IKK γ forms a trimer in solution. The structure is extremely compact with a Rg of 28 Å for a molecular weight (M.W.) of 150 Kda compared with hemoglobin with a Rg of 26 Å for a M.W. of 62 Kda. Hemoglobin is considered as a regular protein molecule in terms of its folding. Biochemical evidence indicates the trimer formation is not due to the concentration effect but natural phenomena. To further study the monomer structure and the regulatory role of the IKK γ we have expressed the IKK γ in two parts. The 'front part' (FE) is consisted of two third of the molecule and the 'back part' (BE) of one third of the molecule. With the scattering curves of these two parts of IKK γ we obtained the models of the FE and BE of the molecule. They both formed dimmers in solution. However, if we put them together they formed a monomer with a distinct structure obtained based on the scattering curve. During our experiment at ILL we experienced a serious technical problem for IKK α as well as for IKK β . They aggregated in solution. We tried using various additives such as high salt, detergents and even IKK γ , still we failed to break down the aggregates. In Juelich we found a way to break down the aggregates through the use of 1M of urea. This concentration of urea keeps the biological activity of these two components intact. This new finding helped us to obtain a preliminary model of IKK β which is consistent with biochemical evidences. All this information is very interesting because so far there is no any structural information on this complex. The results are also quite exciting because they are complimentary to what we had known before in terms of the biological activities. The neutron scattering experiment opens up a horizon for further structural studies of the complex. At this stage for such a huge complex only neutron scattering can offer us useful information on the relationship between structure and function.

Problems

During our December 2005 experiment in Juelich we encountered the following problems:

- 1) The samples of FE and BE of IKK γ had contamination of higher molecular weight aggregates. Therefore, the R_g calculated based on the final model was more than twenty percent lower than the R_g based on the Guinier approximation.
- 2) The samples of IKK α and IKK β formed aggregation which could not be broken up using high salt, detergents and other biochemical reagents except for 1 M urea. The sample still kept its activity in 1 M urea. During the experiment we had used almost twenty percent of the beam time to find out this phenomenon which we did not know before the experiment.
- 3) We know based on the biochemical evidence that front end of IKK γ interacts with IKK α and IKK β . This is considered as the key interaction for the regulatory role of IKK γ . Because of time limit we could only confirm that the interaction existed in our last experiment but we did not have time to collect data for the modeling.
- 4) The concentration of our sample IKK α and IKK β were too low (around 1mg/ml) for the data collection. Therefore the model we obtained needed to be confirmed using higher concentration of the same protein.

Future Prospect

Based on these problems we need to continue our efforts trying to deal with all these problems so that we can obtain precise results and more accurate models of the complex.

Acknowledgement

We would like to thank the Forschungszentrum in Juelich for the success of our experiment. As usual the Forschungszentrum offers us the excellence of instrumentation, experienced and efficient local contacts as well as friendly atmosphere for our experimental success.



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

Proposal number:	KW1-05-058, KW1-06-012, KW1-06-022		
Experiment title:	Thermal composition fluctuation in the PEO/PMMA blend		
Dates of experiment:	05.12. – 07.12.2005 11.03. – 13.03.2006 27.04. – 01.05.2006	Date of report:	31.05.2006
Experimental team: Names	Addresses		
K. Niedzwiedz, A. Wischniewski, D. Richter D. Schwahn, V. Pipich	Institut für Festkörperforschung Forschungszentrum Jülich D-52425 Jülich Germany		
Local Contact:	V. Pipich		

Experimental report text body

Thermal composition fluctuations in the binary PEO/PMMA blend were investigated for five different compositions of PEO homopolymer $\Phi_{\text{PEO}}=0.1, 0.25, 0.35, 0.5$ and 0.75 . The scattering signal was measured heating from room temperature to 160°C and afterwards cooling down with temperature steps of 5K . A hysteresis effect was observed only for the sample with 0.35 PEO content, where the glass transition and crystallization temperature are close. Below the crystallization temperatures the scattering intensity increases by more than two orders of magnitude. In the phase diagram (Figure1) the crystallization temperatures are depicted by black triangles.

Scattering curves for three concentrations (cooling down) are plotted in Figure 2 by filled squares. The scattering cross-section $d\Sigma/d\Omega(Q)$ was analyzed by the random phase approximation (RPA)

$$\frac{1}{d\Sigma/d\Omega(Q)} = \frac{N_a}{\Delta\rho^2} \left\{ \frac{1}{\Phi_{\text{PEO}} V_{\text{PEO}} P_{\text{PEO}}(QR_g^{\text{PEO}})} + \frac{1}{\Phi_{\text{PMMA}} V_{\text{PMMA}} P_{\text{PMMA}}(QR_g^{\text{PMMA}})} - 2 \frac{\chi}{V_0} \right\} \quad (1)$$

with Φ volume fraction, V molecular volume, $P(Q)$ Debye function, R_g the radius of gyration, $V_0 = \sqrt{V_{\text{PEO}} V_{\text{PMMA}}}$ the reference molecular volume, and χ the interaction parameter. In Figure 2 red lines correspond to the fits of the experimental data by Eq. (1) with χ and R_g^{PEO} as adjustable parameters.

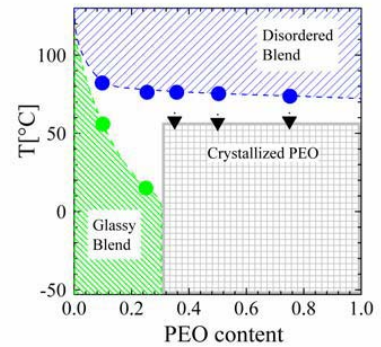


Figure 1. Phase diagram.

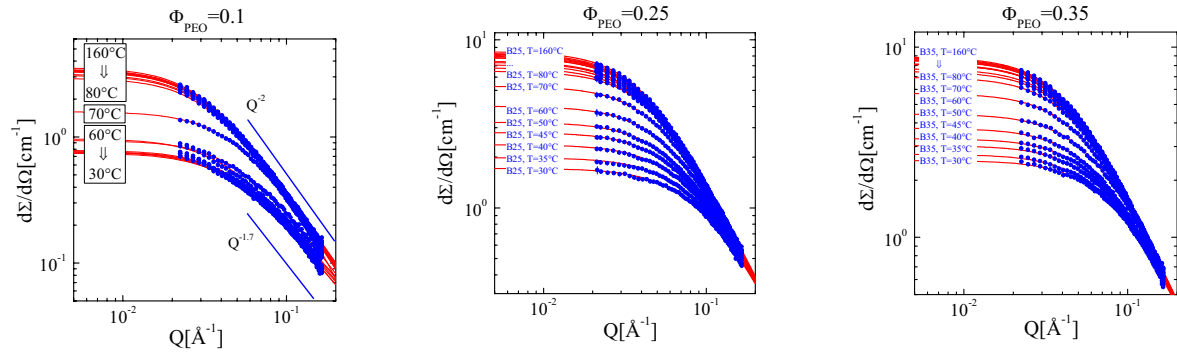


Figure 2. Scattering profiles of $\Phi_{\text{PEO}}=0.1$, 0.25 and 0.35.

In Figure 3 the interaction parameter is plotted as a function of the inverse temperature for three characteristic compositions. Below $\Phi_{\text{PEO}} = 0.3$ no crystallization was observed; but the temperature dependence of χ shows three characteristic temperature regimes: (a) “real” disorder ($T > 85^\circ\text{C}$), where χ is a weak function of temperature (lower critical separation temperature is above 600K); (b) “real” glassy blend ($T < 56^\circ\text{C}$), where composition fluctuations are completely frozen; (c) intermediate temperature range ($85^\circ\text{C} < T < 56^\circ\text{C}$), where interaction parameter becomes “strongly” negative. A strong suppression of the interaction parameter (forward scattering) was observed for all samples. On the phase diagram (Figure 1), temperatures, where the χ -parameter changes behavior, are plotted by blue circles.

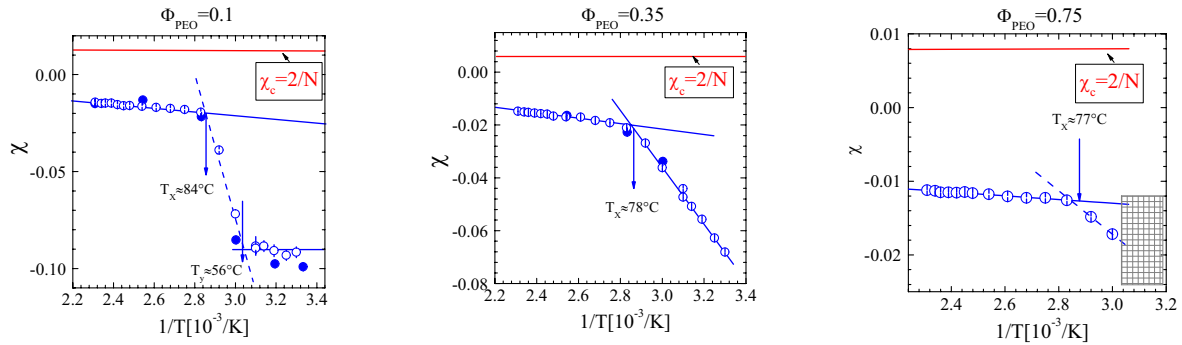


Figure 3. Interaction parameter χ as function of the inverse temperature: $\Phi_{\text{PEO}}=0.1$, 0.25 and 0.75

The blue circles in Figure 4 represent the PEO-PMMA interaction parameter as a function of PEO-content at $T=90^\circ\text{C}$. The χ -parameter is negative for all concentrations. A negative sign of the χ -parameter means that PMMA-PEO interactions are preferred with respect to the PMMA-PMMA and PEO-PEO ones. The huge difference between χ and the critical interaction parameter χ_c (red circles) confirms the remoteness of the critical separation temperature.

In conclusion, during these proposal periods we obtained the phase diagram of the binary polymer blend PEO/PMMA by SANS: crystalline and glassy boundaries were guided; temperature and concentration dependences of the interaction parameter and radius of gyration of PEO-chain were obtained by RPA analysis of SANS data.

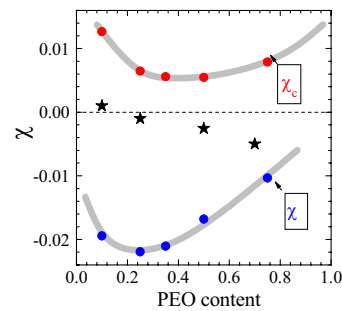


Figure 4. Interaction parameter χ vs. PEO content.



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

Proposal number:	KW1-05-059		
Experiment title:	New Hafnium based catalysts for living olefin polymerisation – Characterisation of final products		
Dates of experiment:	2005-12-1,2,3	Date of report:	2006-06-04
Experimental team: Names	Addresses		
Aizhen Niu Jörg Stellbrink Jürgen Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

Coates et al. [1] reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. However, the kinetics and mechanism of living olefin polymerization is still poorly understood. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization.

In recent SANS experiments we investigated the living polymerisation of poly(hexadienes) using a Titanium catalyst/MAO activator. We found that this system shows some unexpected precipitation after mixing of the individual compounds at low temperatures. I.e. rigorous stirring is required for keeping the catalyst/co-catalyst complex in solution, which is a prerequisite for successful polymerisation. Unfortunately this is not possible in the SANS cell and in particular not in the NMR cell, so that an absolute calibration in terms of sample concentration was not achievable.

Therefore we used another catalyst system to avoid this solubility problem. The new catalyst system contains a Hafnium complex as catalyst and low molecular weight Boron hydride compounds as activator. In the reactor period 2005/08 we performed first test experiments on that system and were able to follow a polymerisation in real-time by insitu-SANS.

Meanwhile we have terminated the polymerisation, cleaned and dried the resulting polymer and characterised it by standard techniques (GPC, NMR). Now the polymer has to be characterised by SANS too, in particular in terms of its radius of gyration, R_g , to allow a quantitative interpretation of the previously performed insitu experiments. Therefore we need to investigate a concentration series in dilute solution (4 concentrations ≤ 0.5 Vol.-%, Zimm-analysis). The molecular weight of the final polymer is approximately 100 000 g/mole.

[1] J. Tian, P. D. Hustad, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 5134.



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

Proposal number:	KW1-05-061		
Experiment title:	Conformation of a cyclic polystyrene within a linear blend in entangled state: characterization of strain dependence		
Dates of experiment:	18.01. – 19.01.2006	Date of report:	17.05.06
Experimental team: Names	Addresses		
Michael Kapnistos Wim Pyckhout-Hintzen	Forth, Crete FZJ		
Local Contact:	Wim Pyckhout-Hintzen		

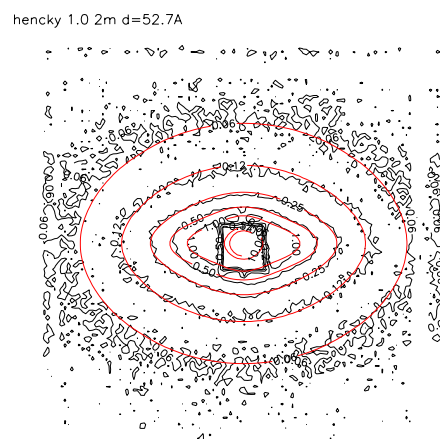
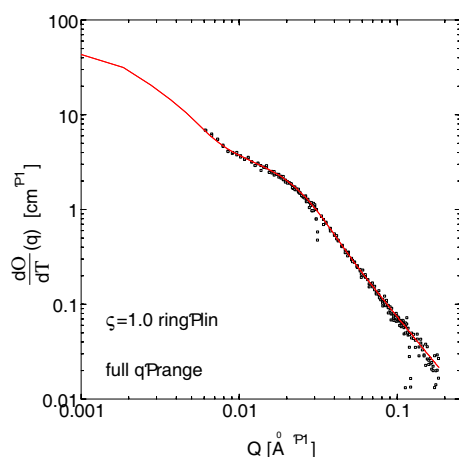
Experimental report text body

SANS studies on a blend of linear polystyrene with a ring-architecture polystyrene were started and in a first stage the deformation behaviour of the ring was studied. The results are to be compared with pure linear blends and linked to the un-usual rheology of ring-linear blends. Samples were stretched in a filament stretching rheometer to hencky strains up to 2 i.e. 700% of deformation. The scattering of a deformed ring with tube confinement was described as for simple linear polymers but modified for the architecture – deformed tube axes with segmental fluctuations – and fits of the full 2d detector could be obtained with only 1 single structural parameter, i.e. the tube diameter. The tube diameter is about 78Å for 170% strain ($\lambda = \text{final_length}/\text{initial_length}=2.7$) (compare to $d(\text{rheology})=90\text{Å}$) and decreases to 54 and 50Å for deformation ratios λ of 4.5 and 7.4. The tube diameter does not seem to be deformed as in the case of polyisoprene. As the ring is 1% in linear, we see the single ring characteristics.

The anisotropic patterns can be calculated in terms of the components along the principal strain axes and the direction cosines e.g. if the strain is parallel to the x-axis, and ϕ is the angle between the strain axis (x) and a direction of the scattering vector q such that $qx = q \cos \phi$ and $qy = q \sin \phi$. A linear tube-constrained structure factor,

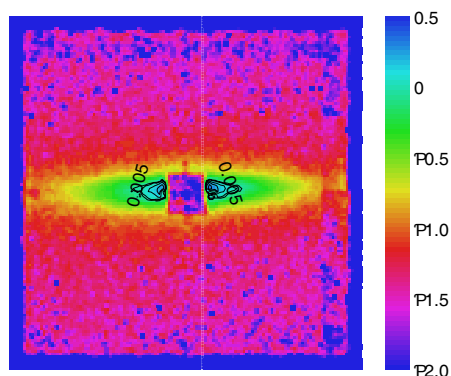
$$S(q, \lambda) = 2 \int_0^1 d\eta \int \prod_{0 \leq x, y, z} \exp(-(qR_g \lambda)^2 (\eta - \eta') - (qR_g)^2 (1 - \lambda^2) \{ \frac{d^2}{2\sqrt{6}R_g^2} (1 - \exp(-\frac{(\eta - \eta')}{d^2})) \})$$

can be generalized for the case of a ring.



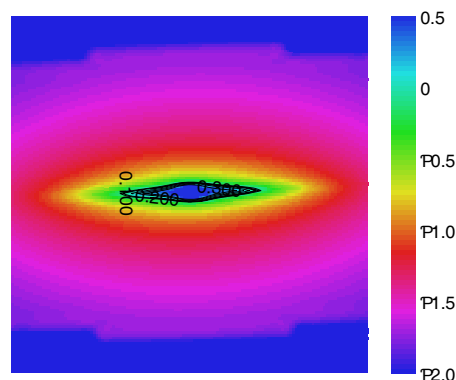
left: isotropic ring scattering + parasitic low scattering. right: deformed ring to $\lambda=2.7$ with full 2d-fit, stretching direction is along vertical direction

hencky 2.0 2m exp



left: experimental scattering at $\lambda=7.4$ effect of 2d-resolution become clear.

hencky 2.0 2m theo



right: best fit. The anisotropy is perfectly matched and

The scattering at low q is due to impurities which are well separated from the ring scattering and allow a perfect determination of the necessary parameters. The modelling of this parasitic scattering was done using a Beaucage powerlaw approach for 2d anisotropic data and it was tested whether the choice of this modelling would lead to different parameters of the ring structure or are identical if the lowest q data are left out. It showed that the same results are retrieved and therefore the situation is of well separated character. This is the first examination of ring segmental parameters at all and a correlation with rheological data could be started.



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

Proposal number:	KW1-05-062		
Experiment title:	Structural studies on the polymer coil relaxation of (linear polystyrene) after exposure to elongational flow		
Dates of experiment:	17.01. – 18.01.2006	Date of report:	14.05.2006
Experimental team: Names	Addresses		
Nielsen, Jens Pyckhout-Hintzen, W	Univ. Copenhagen and Risoe, DK Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	W. Pyckhout-Hintzen		

Experimental report text body

At Riso an elongational flow rheometer was designed, that allows for a controlled elongational flow of constant elongation rate up to a total macroscopic stretch factor $\lambda = \exp(\dot{\epsilon}t) \approx 40$ where t is the time of flow. The possibility to attain of such high stretch factors for well nearly monodisperse linear polymer melts is new and the measurements of stress alone have had a number of important consequences for our theoretical understanding of polymer dynamics. Moreover preliminary SANS experiments have revealed that the coil stretching under such conditions are more than 50% of the fully extended tube when exposed to elongation rate of $\dot{\epsilon} = 0.1 \text{ s}^{-1}$.

A recent modification to our rheometer allows us to stop the flow abruptly within the centre of the sample, dynamically controlling the sample diameter in a electronic feed-back loop. Using the time-temperature superposition this gives access to controlled pseudo-real-time relaxation studies with high resolution within time ranges from well below the Rouse time to far beyond the reptation time. Preliminary stress-relaxation function has already been measured in such experiments, and will be measured as well for all the samples used in the SANS experiments.

For the SANS studies the polystyrene samples are quenched well below the glass temperature within time scales much lower than the Rouse time. To eliminate possibly fast relaxation near the chain ends, only the centre part of the polymer chains are deuterium labelled which gives us further a length scale more easily accommodated by the SANS facility.

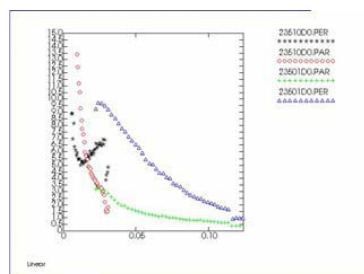
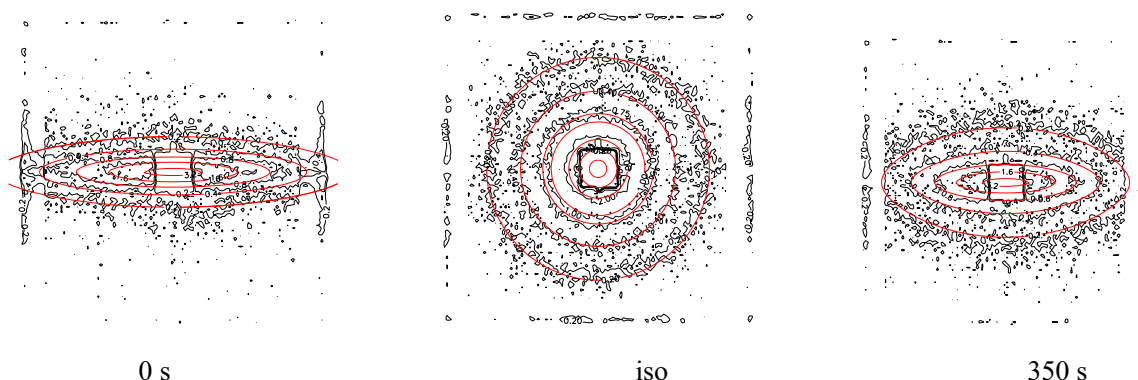
The results are expected to provide new information on the relaxation of linear polymer chains from a well defined but highly stretched initial state. In particular the results enable the testing of the classic separation of relaxation into a fast mode of relaxation of stretch along a primitive path (by Rouse dynamics) and a slow relaxation of orientation of effective tube elements (by reptation) as was seen recently by Blanchard et al in a polyisoprene system.

Experimentally, the investigation was very difficult as the resulting samples after stretching in the rheometer were very thin and needle-like centrally where the beam is placed. Special diaphragms were made of 8mm slit length and width of 0.5mm to cover the whole sample. Counting rates were as low as 20cps at low q and never reached more than 500 cps at high q . Therefore, it puts an enormous strain on the machine in that all additional corrections from backgrounds and collimation must be known accurately. It proved that the smallest q 's were not fittable and only high q are available of average quality.

The purpose of the experiment – to analyze the radius of gyration in the highly non-linear state and the tube diameter of the chain – was not completely reached as the high q data both are sensitive to the strain of the chain as well as primarily the segmental fluctuations. It would have been fruitful to obtain former strain dependence from small q fittings and keep it constant for the determination of the diameter which itself could be strain dependent by the way. The evolution of the anisotropy is clear, however, and more external information e.g. for the microscopic strain are needed to yield the full parameter set.

More-over, the scattering on the deformed pure triblocks in order to gain intensity and to take profit from the sensitivity of a correlation hole effect to strain were also not ideal as the expected peaks did not show up due to several possible reasons: polydispersity in the blocks, degradation due to the very stringent conditions of preparation to give mixtures of labelled components.

Therefore a final evaluation of the data is not yet possible and awaits combination with other techniques. Some preliminary data fittings are shown here: on the left, the 0s data (virtually no relaxation) are described using the Warner-Edwards model with tube diameter 26A which is much lower than the isotropic one from the plateau modulus. On the right, the relaxed sample with $t=350$ s shows increased isotropy and is fairly well described by roughly a double diameter, i.e. 72A. Compared in the middle is a 2D fitting of the isotropic set with a Debye curve from which the reference R_g was extracted.



Pure triblock peaks: besides resolution effects, an unexpected upturn at $q \sim 0.01$ is visible which is a signature of impurities or degradation..



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

Proposal number:	KW1-05-064		
Experiment title:	Hierarchical structure of silica and Carbon Black 2		
Dates of experiment:	15.01. – 17.01.2006	Date of report:	01.06.2006
Experimental team: Names	Addresses		
G. J. Schneider V. Vollnhals D. Göritz	Institut für Physik Universität Regensburg 93040 Regensburg Gerald.schneider@physik.uni-regensburg.de		
W. Pyckhout-Hintzen	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Dr. W. Pyckhout-Hintzen		

Experimental report text body

1. Abstract

Carbon Black is the most important filler in tire industry. However the correlation between structure and mechanical properties of the filled elastomers has not been understood up to now. The purpose of this report is to show discrepancies between the results of neutron scattering experiments and the structural parameters described by industrial norms.

2. Introduction

Carbon Black is the filler of choice to improve the properties of elastomers. Nowadays different Carbon Blacks are distinguished by industrial norms (ASTM classification). For the purpose of a short overview tab.1 summarizes some characteristics for the Carbon Blacks N 326, N 330, N 339 and N 375. For efficient development of fillers for rubbers the linkage from structure, described by the norms, to the improvement of mechanical properties is of large interest. The purpose of this report is to show the difference between the parameters listed in tab. 1 and the structure of the Carbon Blacks determined by neutron scattering experiments.

4. Experiment and Theory

By measuring the scattered intensity as a function of scattering length q ($q = 4\pi/\lambda \sin(\theta/2)$), and plotting the result in a log-log-plot, typically a curve with different slopes can be observed. Whereas the structure size can be extracted from the position of the crossover between two regions with different slopes, the slope itself gives

	CTAB surface area [m ² /g]	DBP absorption [ml/(100 g)]	Compressed DBP absorption [ml/(100 g)]
N 326	83	72	68
N 330	82	102	85
N 339	92	120	104
N 375	96	114	96

Tab. 1: Characteristics of the investigated Carbon Blacks. CTAB surface area according to ASTM D 3765. DBP absorption according to ASTM 2414; Compressed DBP absorption according to ASTM D 3493-90.

information about the structure or to be more exact, the mass fractal dimension or the surface roughness, i. e. the surface fractal dimension, depending on the length scales considered.

3. Results

Figure 1 shows the scattered intensity as a function of the scattering length, for different Carbon Black samples. For the purpose of a better comparison the intensity values are normalized, therefore the intensity is in arbitrary units. Considering first the q -values larger than 0.2 nm^{-1} the almost identical slopes are evident. For values smaller than $q = 0.2 \text{ nm}^{-1}$ each curve shows a crossover to a second slope. For the regime $q < 0.06 \text{ nm}^{-1}$ the scattering diagram reflects the mass fractal dimension. The change of the slope in this regime should reflect the dependence of the values for the different Carbon Blacks listed in tab. 1. However, as one can see in fig. 1, there is no systematic dependence.

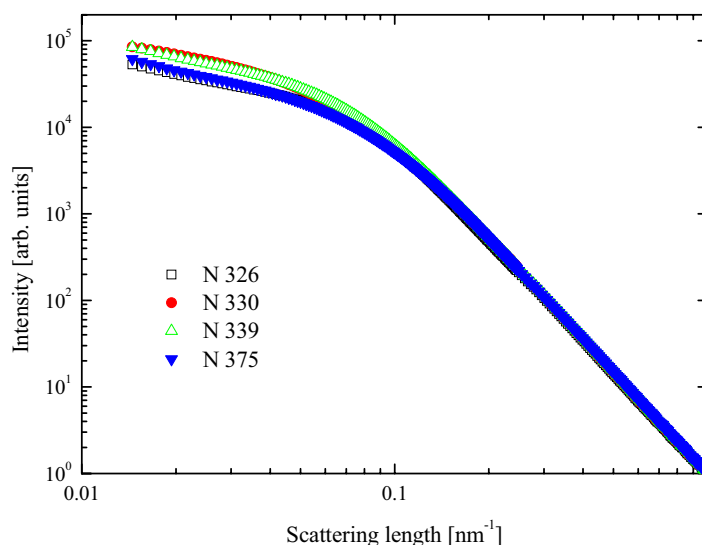


Figure 1: Intensity as a function of scattering length for different Carbon Black samples.

4. Conclusion

It was shown that the dependence of the structure from the type of Carbon Black found by means of scattering experiments disagrees with the characteristics defined by the norms. Since Carbon Black determines the mechanical properties of elastomers to a great extent, this result is important for future developments of high performance rubbers used in industry.



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

Proposal number:	KW1-05-065		
Experiment title:	Final stages of “living” anionic polymerisation investigated by contrast variation SANS		
Dates of experiment:	13.01. – 15.012.2006	Date of report:	03.06.2006
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jürgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Anionic polymerisation is one of the key polymerisation techniques yielding well defined polymers both with respect to molecular weight distribution as well as architecture¹⁾. In recent experiments we were able to relate in detail monomer conversion and initiation processes of “living” anionic polymerisation with structural details combining in-situ high resolution ¹H-NMR and in-situ small angle neutron scattering (SANS). The combination of NMR and SANS opens a new realm of research into polymerisation processes, which appear to reveal completely new aspects of this polymerisation mechanism. With this proposal we ask for 3 days beam time at KWS-1 in order to determine by means of contrast variation the time dependent composition of intermediate species present in the initiation period. These “cross aggregates”, mixed aggregates of growing polymer chains and unreacted initiator molecules, seem to crucially determine the active centre reactivities in the early stages of these living anionic polymerisations. Clear evidence for the existence of cross aggregates can be obtained by performing time-resolved SANS experiments under different contrast conditions. Matching either the initiator or the growing polymer chain by selective use of protonated/deuterated compounds will resolve all the structural details and composition of intermediate species present in the initiation period. It is essential to do the experiments with different butyllithium concentrations, that means different molecular weights to understand the increasing reactivity of butyl lithium with increasing concentration.

This experiment is a continuation of an experiment recently started using D22 (ILL). There we followed by insitu SANS the structure formation in the initiation period of “living” anionic polymerisation using contrast variation. However, due to the limited beam time we were only able to follow the polymerisation for 1 ½ days. After the experiment all samples were quenched to -78°C and stored at this temperature. We have shown that the polymerisation no longer progresses under these circumstances.

In detail the following time-resolved experiments should be performed: For in total 6 different samples, i.e. 3 initiator concentrations at 3 contrasts (full, polymer and butyllithium contrast) the scattering profiles were followed in real-time for two days, see Fig. 1.

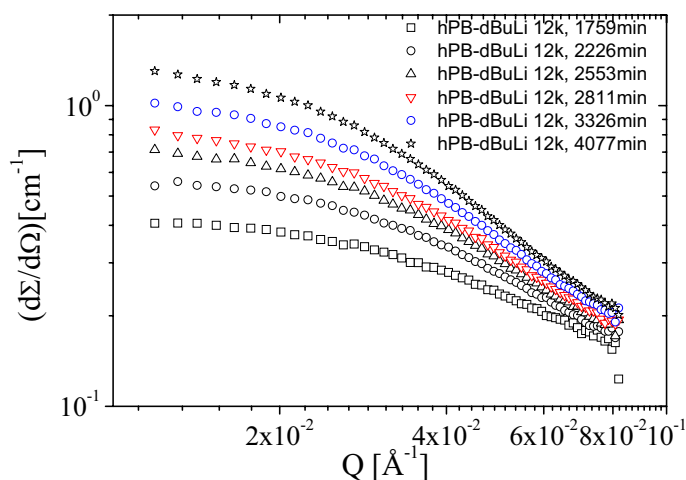


Fig. 1 Scattering profiles obtained by real time SANS from KWS-1, the later stages of living anionic polymerization of butadiene in d-heptane at 8°C using d-tert-butyllithium as initiator. The scattering contribution of solvent was not subtracted.

References:

1. M. Szwarc, M van Beylen, Ionic Polymerization and Living Polymers, Chapman&Hall: N.Y./London (1993)
2. A. Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, A. Radulescu, D. Richter, B. W. König, R. P. May, L. J. Fetters, J. Chem. Phys., **122**, 134906, (2005)



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

Proposal number:	KW1-06-001, KW1-05-041, KW1-05-047		
Experiment title:	Chain conformation in novel, natural-synthetic hybrid block copolymers		
Dates of experiment:	26.09. - 28.09.2005 11.11. - 13.11.2005 16.02. - 18.02.2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Dr. L.J.R. Foster ^{1,2} Dr. D. Schwahn ² Dr. V. Pippich ²	¹ Bio/polymers Research Group, School of Biotechnology and Biomolecular Sciences, University of New South Wales, Sydney NSW 2052, Australia. ² Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, 524425 Jülich, Germany		 Bio/polymer Research Group
Local Contact:	Dr. D. Schwahn		

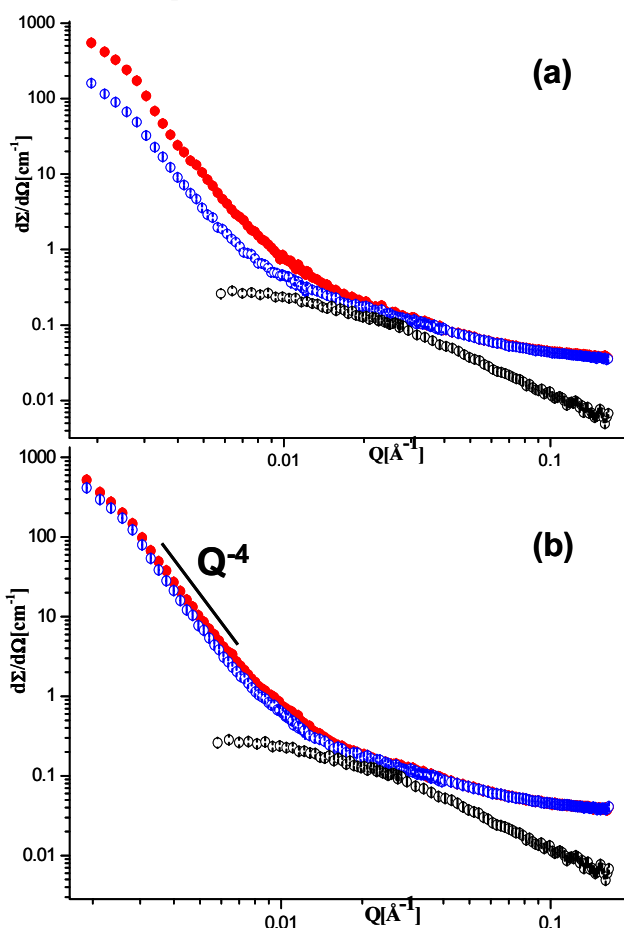
Experimental report text body

Introduction Polyhydroxyalkanoates (PHAs) are a family of biopolyesters synthesized by a wide range of microorganisms. The most common of these biopolymers is Polyhydroxybutyrate (PHB), which has received considerable interest as an environmentally friendly bioplastic and as a biomaterial for biocompatible medical implantation devices. PHB however, is just one member of a family of biopolymers possessing in excess of 105 different monomeric components. These novel biopolymers have material properties ranging from the rigid and highly crystalline to flexible, rather amorphous and elastomeric [1]. Another member of interest is Polyhydroxyoctanoate (PHO). PHB and PHO are representative members of PHAs possessing short and medium chain length substituents in the side chain (*sc*/PHA and *mc*/PHAs).

We have recently synthesised natural-synthetic hybrids of PHB and PHO by 'end-capping' hydrophobic PHA chains with hydrophilic diethylene glycol (PHB-DEG and PHO-DEG respectively) [2]. The family of PEGs has a wide range of members varying in molecular mass and structure. A number of biocompatible members have important biomedical functions such as organ and tissue preservation [3]. Material surfaces modified by covalent attachment of PEG chains are resistant to cell and protein adsorption [4]. During solvent casting PHA-PEG hybrids self-assembled into ordered microporous arrays [5]. These microporous films, by virtue of their biocompatible composition and morphology, have the potential to serve a range of biomedical and biotechnological applications.

The objective of this research is to elucidate the influence of the relatively small hydrophilic group in these hybrids on polymer chain conformation, with a particular reference to their ability to form microporous films. In this regard, a synthetic block copolymer: Polystyrene-*b*-polydimethylacrylate which forms highly ordered microporous films is used as a positive control. Thus, based on electron microscopy studies, the degree of organisation in microporous films increases in the following sequence: PS-PDMA > PHB-DEG > PHO-DEG.

Experimental A series of SANS experiments were carried out to investigate the conformation of natural and hybridised PHA chains in the presence of micro-quantities of water (1% v/v). Deionised water was added to quartz cuvettes and vigorously mixed prior to placing in the neutron beam – SANS experiments were performed with biopolymers in solutions using deuterated chloroform and deuterated methylene chloride at concentrations range of 10 and 40 mg/ml. Scattering data was collected upon mixing and after standing for 10–12 hours. Samples were then remixed and low Q scattering collected every 20 minutes for 10 hours.



Results & Discussion Previous results showed an apparent failure of the DEG groups to influence chain conformation in solution. This is unsurprising given the difference in molecular mass between the natural and synthetic groups (approximately 600:1). However, the introduction of micro-quantities of water (1% v/v) followed by vigorous mixing, had noticeable visual effects. For example, while the chloroform solutions of PHO rapidly partitioned into two phases, the solutions of PHO-DEG appeared to form a stable microemulsion.

Figure 1: Scattering data for solutions of PHO and PHO-DEG in deuterated chloroform (10 mg ml^{-1}) after addition of 1% (v/v) water and vigorous mixing, (a) PHO and (b) PHO-DEG, ($\circ$) data from 1st and ($\bullet$) 10th hour of scattering and ($\circ$) PHO/PHO-DEG in absence of H_2O .

As an example of the experimental data acquired, Figure 1 illustrates the change in scattering patterns of the PHO and PHO-DEG biopolymer solutions with the addition of water, which can be readily observed at low Q with a best visual estimate of -4 . At 10 mg ml^{-1} this low Q scattering of PHO decreased significantly with time, suggesting the gradual partitioning of water from the PHO solution (Figure 1a). In contrast, PHO-DEG solution at a similar concentration showed little change in scattering after standing for 10 hours (Figure 1b). Increasing the PHO-DEG concentration to 40 mg ml^{-1} apparently facilitated this ‘microemulsion’ effect, with the scattering increasing with standing.

Thus, our results suggest the incorporation of water into the PHO-DEG solution and its long term stability, while in a solution of PHO it gradually partitions. Thus, the small hydrophilic DEG may facilitate some degree of self-assembly and suggest that key factors in microporous film formation may be chain conformation and mobility.

- [1] Steinbüchel, A. In: Rehm H-J, Reed G, editors. *Biotechnology*. Weinheim, Germany: John Wiley & Sons, **1996**.
- [2] Sanguanchaipaiwong, V; Gabelish, CL; Hook, J; Scholz, C. & Foster LJR. *Biomacromolecules* **2004**;5(2):643.
- [3] Harris JM. *Poly(ethylene glycol) chemistry: biotechnical and biomedical applications*. New York, USA: Plenum **1992**.
- [4] Inada Y, Matsushima A, Kodera Y, Nishimura H. *J. Bioact Compat Polym.* **1990**;5:343.
- [5] Foster, LJR; Sanguanchaipaiwong, V; Gabelish, C. & Hook, J. *Polymer* **2005** 46(17):6587-6594.



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

Proposal number:	KW1-06-002		
Experiment title:	Final stages of “living” anionic polymerisation investigated by contrast variation SANS		
Dates of experiment:	22.02. – 24.02.2006	Date of report:	02.06.2006
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jörgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Anionic polymerisation is one of the key polymerisation techniques yielding well defined polymers both with respect to molecular weight distribution as well as architecture¹⁾. In recent experiments we were able to relate in detail monomer conversion and initiation processes of “living” anionic polymerisation with structural details combining in-situ high resolution ¹H-NMR and in-situ small angle neutron scattering (SANS). The combination of NMR and SANS opens a new realm of research into polymerisation processes, which appear to reveal completely new aspects of this polymerisation mechanism.

The “cross aggregates”, mixed aggregates of growing polymer chains and unreacted initiator molecules, seem to crucially determine the active centre reactivities in the early stages of these living anionic polymerisations. Clear evidence for the existence of cross aggregates can be obtained by performing time-resolved SANS experiments under different contrast conditions. Matching either the initiator or the growing polymer chain by selective use of protonated/deuterated compounds will resolve all the structural details and composition of intermediate species present in the initiation period. It is essential to do the experiments with different butyllithium concentrations, that means different molecular weights to understand the increasing reactivity of butyl lithium with increasing concentration.

With this proposal we ask for 2 days beam time at KWS-1 in order to characterize the final living and the terminated stages of anionic polymerisation by means of contrast variation.

This work is a continuation of experiments recently started using D22 (ILL) and KWS-1. In D22, we followed by insitu SANS the structure formation in the initiation period of “living” anionic polymerisation using contrast variation. After the experiment all samples were quenched to -78°C and stored at this temperature. We have shown that the polymerisation no longer progresses under these circumstances. In the last experiment performed at KWS-1, the later polymerization stages were monitored at 8°C from reaction time 2000 min to 15000 min.

In detail , for in total 6 different samples, i.e. 3 initiator concentrations at 3 contrasts (full, polymer and butyllithium contrast), the final living and the terminated stages were measured with sets up D20C20, D8C8 and D4C4, see Fig. 1.

References:

1. M. Szwarc, M van Beylen, Ionic Polymerization and Living Polymers, Chapman&Hall: N.Y./London (1993)
- A. Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, A. Radulescu, D. Richter, B. W. König, R. P. May, L. J. Fetters, J. Chem. Phys., **122**, 134906, (2005)

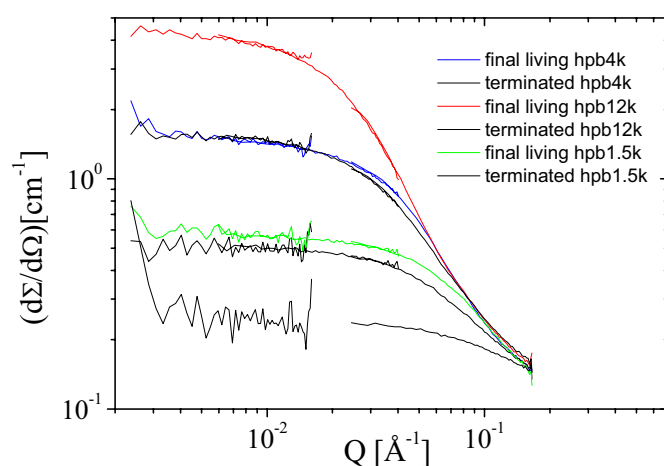


Fig. 1 SANS profiles of final living and terminated chains of polybutadiene with d-tert-butyllithium as initiator.



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

Proposal number:	KW1-06-003		
Experiment title:	Chain conformation of syndiotactic polypropylene		
Dates of experiment:	25.-26.02.2006	Date of report:	01.06.2006
Experimental team: Names	Addresses		
V. Pipich M.Zamponi	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	V.Pipich		

Experimental report text body

Syndiotactic polypropylene (s-PP) is a very interesting polymer for dynamical investigations since it is a very stiff polymer but at the same time has a low segmental friction (see also BSS_06_001). As a preparatory experiment the stiffness parameter (C_∞) and its temperature dependence shall be determined by static measurements.

The static structure factor for 3 different temperatures in the range of the dynamical experiments (463K, 473K, 483K) and three different concentration of a few percent (1%, 2%, 3%) deuterated s-PP in a protonated s-PP matrix have been measured (molecular weights 158 kg/mol resp. 136 kg/mol). The experiments have been performed in vacuum at a neutron wavelength of 7 Å covering a q-range of about 0.002-0.2 Å⁻¹.

For all the samples no temperature dependence of the static structure factor in the limited temperature range have been observed (fig.1). At low q-values all samples displayed a stronger scattering intensity than expected (fig.2). This scattering pattern follows a q-dependence $\sim q^{-4}$, indicating that it probably stems from scattering on small bubbles within the samples.

The concentration dependent scattering intensity can be accounted for by subtracting the incoherent background level and dividing the resulting data by the volume fraction $\phi(1-\phi)$ for each sample. All data then agree, except for the excess forward scattering at low q. Therefore the radius of gyration is concentration independent and can be fitted for all three samples simultaneously.

The data are well described by a sum of a Debye function with background and a function $A \cdot q^{-4}$ to describe the forward scattering. The constants for background and forward scattering and the radius of gyration are fitted (lines in fig.2). The resulting radius of gyration is $R_g=165 \text{ \AA}$, giving a segment length of $l=7 \text{ \AA}$, which is close to the literature values of about $7.6 \text{ \AA}$ (Jones et al., Macromolecules 2002). With the relation $l^2 = C_\infty n l_0^2$, n the average number of main-chain bonds per monomer (2) and l_0 the average bond length ($1.54 \text{ \AA}$), C_∞ is estimated to be 10.5 (literature value 9.12).

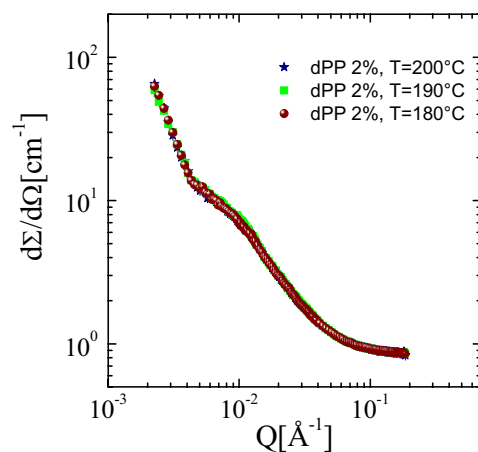


Fig.1: Temperature dependent scattering intensity for one sample.

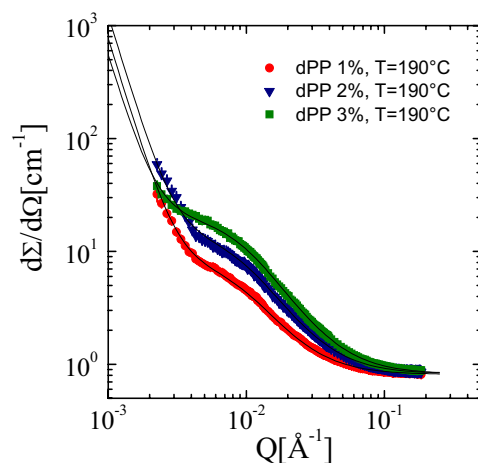


Fig.2: Concentration dependent scattering intensity for one temperature.
Lines are a simultaneous fit of the different concentrations.

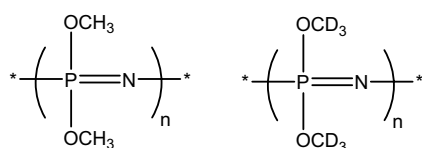


Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-06-004		
Experiment title:	Investigation of chain dynamics in poly(bismethoxyphosphazene)		
Dates of experiment:	09.02.2006 – 11.02.2006	Date of report:	25.05.2006
Experimental team: Names	Addresses		
Yunus Karatas Prof. Dr. Hans-Dieter Wiemhöfer	Institut für Anorganische und Analytische Chemie Westf. Wilhelms-Universität, Corrensstr. 30 48149 Münster		
Local Contact:	W. Pyckhout-Hintzen, R. Zorn		

Experimental report text body

Polyphosphazenes which contain phosphor and nitrogen atoms joined by formally unsaturated bonds represent one of the largest classes of inorganic polymers, because a wide variety of side chains can be used to modify and fine tune both the chemical and physical properties of these polymers. One of the possible future applications of these inorganic polymers is as solid polymer electrolytes in lithium batteries, where these materials serve as solvents for salts acting as ionic conductors.



Many techniques have been applied to the characterization of polyphosphazenes up to now, however neutron scattering is not yet known for them. Therefore, first neutron scattering experiment have been performed with the model polymers (left) in order to understand solution and melt properties of the polyphosphazenes. The next step of the experiment was to look for the influence of salt on the melt conformation of the polymers.

SANS experiments were performed with the KWS1 spectrometer at the FRJ-2 Dido reactor in Jülich, Germany. The reactor runs at 20 MW and has a D20 moderator. Data were collected at distances sample-to-detector of 2, 8 and 20m which lead to an equivalent scattering vector range q between 0.002 and $0.2 \text{ \AA}^{-1}$ approximately using a neutron wavelength $\lambda = 7 \text{ \AA}$ with a wavelength spread $\Delta\lambda/\lambda = 0.20$.

Polymer Solutions in DMF-d6: Dilute solutions were characterized using the Zimm extrapolation method (Figure 1). The radius of gyration and second virial coefficient values were extracted from double extrapolation of the Zimm's plot. These results ($R_g = 144.7$ and $M_w = 95000$ g/mol) were comparable to the results found by GPC in our lab. The A_2 value found for the polymers in DMF at room temperature ($8.6E-4$) is typical for polymers in a good solvent. The slope of 2 and 8 m data as shown in Figure 2 is 1.647 which is in exact agreement with the expected excluded volume exponent predicted by Flory's theory.

Polymer and salt-in-polymer in molten state: Polymer melts were prepared by mixing 5 vol-% of the deuterated polyphosphazene with 95 vol-% of non-deuterated one. 5 and 10 wt-% $LiSO_3CF_3$ containing salt-in-polymer systems were investigated additionally using the same polymer composition of the melt. The

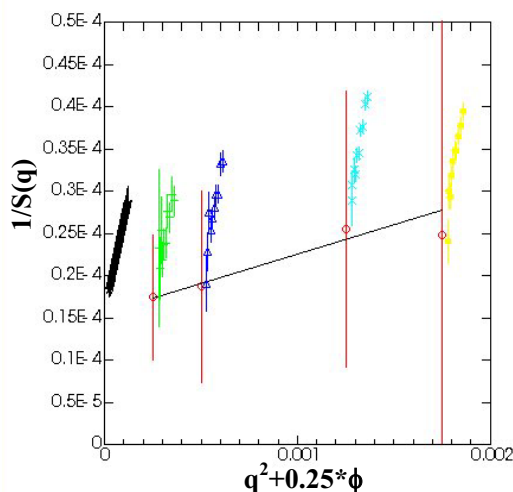


Figure 1. Zimm plot for polymer dissolved in DMF-d6

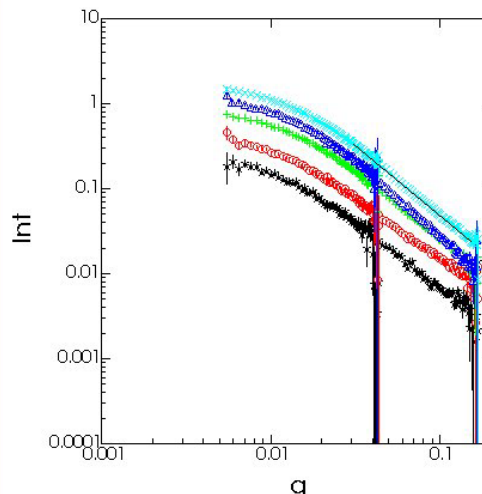


Figure 2. Scattering intensity of polymer solution as a function of wave factor

scattering at low q in the blends is from the polymer. It can be excluded from the observed q -dependence that it is a 'simple' mixing effect or Flory-Huggins interaction term between the deuterated and non-deuterated polymer. The data show a typical levelling-off in the same way as the solutions (usable data: $q > 0.007 \text{ \AA}^{-1}$), below this it goes up.

Summary: R_g values were calculated using both the Guinier fitting and Schultz-Zimm-Flory distribution. R_g goes down a little from 85 to 83 if T is increased from 12.5 to 60.6°C polymer melt, which is virtually constant for salt-in-polymer systems (Table 1). These results show that the salt added to the melt has no effect on the conformation of the polymer. Increasing the temperature didn't change the behaviour. That means diffusive transport of the ions is dominating for this particular polyphosphazene system.

Table 1. Schultz-Zimm-Flory distribution

Name	T	Phi	Rg	Rg _n	Bgr	Epsilon
Polymer melt	12.5	0.89	85	61.9	0.903	1.01
Polymer melt	36.6	0.84	83.6	60.1	0.931	1.02
Polymer melt	60.6	0.85	83.2	61.9	0.925	1.01
5 wt-% salt-in-polymer	12.5	0.78	84.5	62.0	0.86	1.01
5 wt-% salt-in-polymer	36.6	0.73	84.4	59.4	0.89	1.02
5 wt-% salt-in-polymer	60.6	0.73	85.1	60.6	0.90	1.02
10 wt-% salt-in-polymer	12.5	0.69	83.1	62.0	0.85	1.00
10 wt-% salt-in-polymer	36.6	0.65	84.2	60.5	0.87	1.02
10 wt-% salt-in-polymer	60.6	0.66	84.4	62.5	0.87	1.01
						<1.01>



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

Proposal number:	KW1-06-005		
Experiment title:	A characterization of Fe₃O₄ particles in solution		
Dates of experiment:	11.02. – 13.02.2006	Date of report:	15.05.2006
Experimental team: Names	Addresses		
Pyckhout-Hintzen, W	FZJ		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

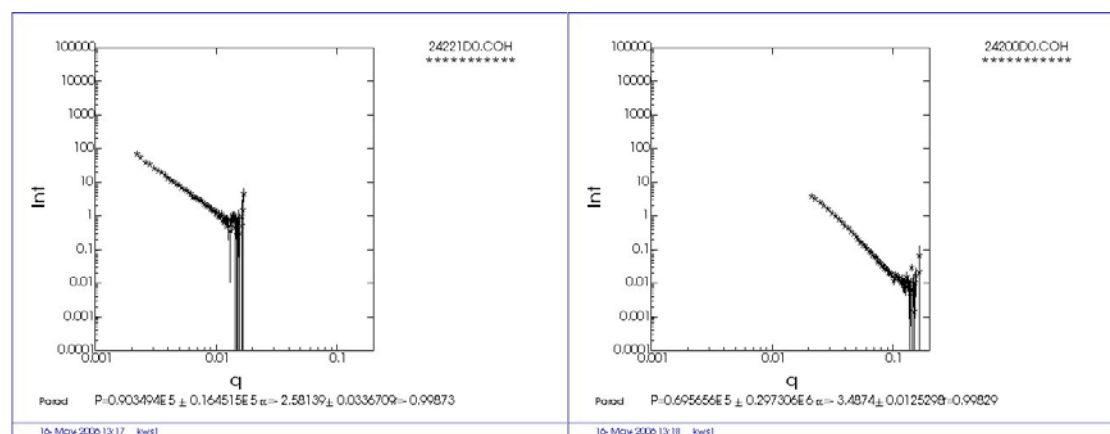
Smart materials have seen increased interest lately. In the following experiment we wanted to characterize a commercial Fe₃O₄ sample, which was dispersed in water and which could be modified afterwards to be blended with homopolymers if the structure is suitable. Therefore the emphasis is on the clustering behaviour and sizes of the primary nanoparticles and the aggregated structures.

Before any blending with a polymer can be tried, a prior characterization of the particle is required. According to the company who synthesized and sells chemically-modified nanoparticles for all kinds of purposes (Micromod Rostock, D) the diameter is about 200nm for the aggregate with size-polydispersity <1.1. SANS measurements of the solution should reveal all necessary structural details of the particle, its fractal structure as well as the structure factor in the case of more concentrated solutions.

The choice fell on this prepare due to the density: as it is 5g/ml this should not be visible in the nanometer scale. Data were obtained from diluting the original solution of concentration 25mg/ml of Fe₃O₄ down to 1/20 of the stock solution in order to isolate eventually the structure factor. It shows experimentally that there is no measurable contribution of $S(q)$ whatsoever and perfect scaling with volume fraction of magnetite is reached.

An evaluation of the log-log intensities yields following preliminary parameters of the system: clearly clusters with mass fractal dimension of about 2.5-2.6 are found as is typical for precipitated silica fillers e.g. or carbon black. The surface fractal exponent is also very similar and is found to be $6-3.5=2.5$ where the q -dependence is $q^{-3.5}$. If one assumes the particles to be flat and not fractally, i.e. the surface scattering is described is q^{-4} then the radius of the primary particles which is extracted is about 27.5nm or diameter about 60nm.

This is in fair agreement with the size of Fe₃O₄ crystallites which could be the building blocks. This is according to the company of the order of 15-20nm. Further descriptions have not yet been performed nor could a blending with polymer be tried in the lack of time.



Left: Mass fractal of the clusters is 2.6.

Right: surface fractal dimension is 2.5 roughly.

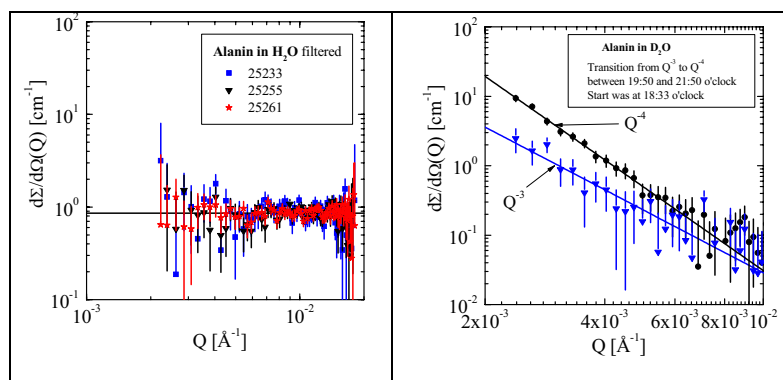


Experimental Report of Neutron Scattering Experiments at the FRJ-2 Reactor

Proposal number:	KW1-06-009		
Experiment title:	DL-Alanine Mesocrystal formation		
Dates of experiment:	13.03. - 15.03. 2006	Date of report:	18.05.06
Experimental team: Names	Addresses		
	PD Dr. habil. Helmut Cölfen Max-Planck-Institute of Colloids and Interfaces Colloid Chemistry Am Mühlenberg 1 14476 Golm Germany Tel: --49 331 567-9513 Fax: --49 331 567-9502		
Local Contact:	Dietmar Schwahn		

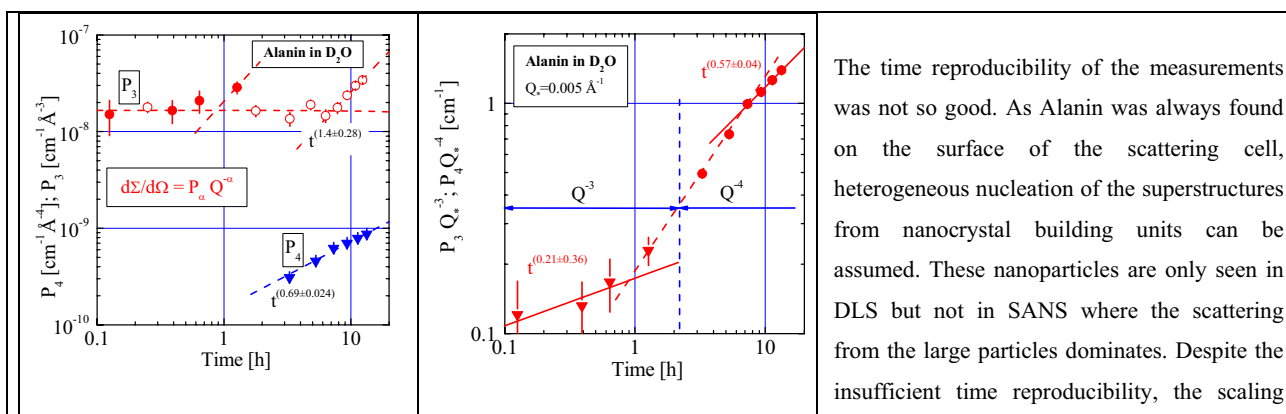
Experimental report text body

DL-alanine was found to form so called mesocrystals, which are superstructures of nanoparticles in crystallographic register. It is unclear how these highly aligned structures form and also, the inner structure of the well faceted mesocrystals is largely unknown. Therefore, a SANS experiment was carried out and performed on different scattering contrasts.

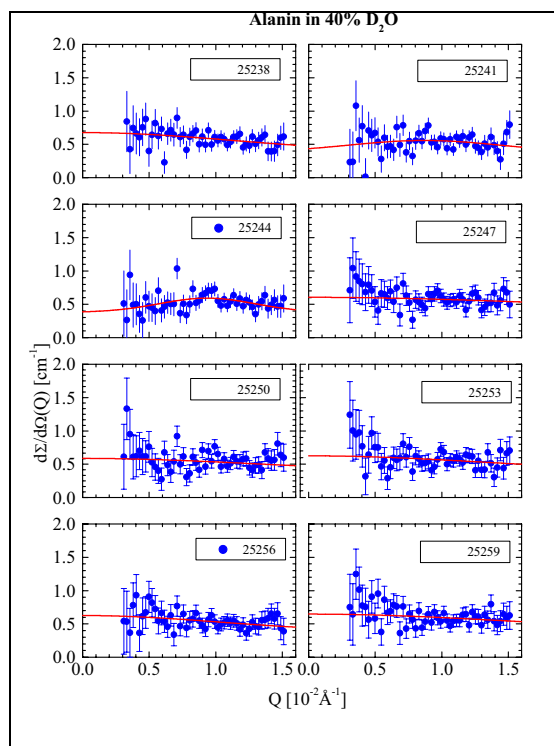


No coherent scattering from alanin was visible in H₂O, probably the incoherent scattering from H₂O was too large. On the other hand in D₂O coherent scattering was visible, showing large particles of at least μm particle size, whose large Q tails showed Q^{-3} power law behavior in the beginning and later a transition to Q^{-4} behavior characteristic for compact particles. This transition took place two hours after starting the reaction.

This observation is consistent with DLS and electron microscopy results, which show small precursor particles in solution particles of ca. 70 nm size and large particles $> 10 \mu\text{m}$. The latter are the nanoparticle superstructures, which are seen in SANS. The SANS result indicates that the μm -sized mesocrystals have an inner structure composed of nanoparticles, which fuse together to finally form compact Alanin single crystals.



The time reproducibility of the measurements was not so good. As Alanin was always found on the surface of the scattering cell, heterogeneous nucleation of the superstructures from nanocrystal building units can be assumed. These nanoparticles are only seen in DLS but not in SANS where the scattering from the large particles dominates. Despite the insufficient time reproducibility, the scaling behaviour is found constant (left figure, open and closed circles) so that it can be considered to be reproducible. An increase in the amplitude of the surface is indicated by the increase in P_4 in the left plot and the marked increase in P_3 shows the growth of the μm particles – most likely from the ca. 70 nm precursor particles detected in solution by DLS. The fusion of the nanoparticles inside a micrometer sized crystal to a compact single crystal without inner structure could be followed with a relatively sharp transition from Q^{-3} to Q^{-4} behaviour around 2h. (right figure). In 40% D₂O aqueous solution which is the matching condition for alanin no scattering should be visible. Scattering from heterogeneities of radius of gyration of about 110 Å is found nearly independent of time. This value is smaller than the hydrodynamic radius variation of 35 nm of the 70 nm primary particle building units detected in DLS. The reason for this discrepancy is still unknown.



Summarizing, the SANS experiments showed clearly, that mesocrystals have an inner structure. This structure compacts with time to a large crystal without inner structure (a single crystal). Although the primary nanoparticle building units could not be detected in solution, as their concentration was too low and/or was hidden behind the scattering from the large units to be detected, the SANS experiments give clear evidence, that the detected large (> 1 micrometer) crystals are composed of subunits, which later became a compact structure. A time evolution of this process could be evidenced. This is an important finding, as it underlines an alternative crystallization pathway – the formation of a single crystal from nanoparticle building units via a mesocrystal intermediate rather than the textbook view, which considers single crystal formation via growth by attachment of single molecules to a critical crystal nucleus.



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

Proposal number:	KW1-06-013		
Experiment title:	Micellar re-structuring after interfacial tension jump		
Dates of experiment:	24.3. 2006 18.-19.4. 2006	Date of report:	06.06.2006
Experimental team: Names	Addresses		
J. Stellbrink	IFF, FZ Jülich, D-52425 Jülich, Germany		
Local Contact:	J. Stellbrink		

Experimental report text body

Recently we investigated the self assembly of the amphiphilic block copolymer poly(ethylenepropylene)-poly(ethyleneoxide), $M_{w,PEP} = 1000 \text{ g/mol}$, $M_{w,PEO} = 20000 \text{ g/mol}$ (PEP1-PEO20), in different water/dimethylformamide mixtures by small angle neutron scattering (SANS) [1]. The solvent composition could be used to precisely adjust the functionality of these star-like micelles, but also the intermicellar exchange kinetics [2]. In aqueous solution no exchange of individual block copolymers between different micelles could be observed, even at elevated temperatures, i.e. all micelles are completely kinetically frozen. On the other hand, in water/DMF mixtures with a mole fraction $x_{dmf} \geq 0.25$ the exchange of individual block copolymers is in the minute range and follows a logarithmic time dependence [2].

In addition we used star-like PEP-PEO micelles as an analogue of regular star polymers (*ultra-soft* colloids) to compare the experimental equilibrium phase diagram in the packing fraction (η) / functionality (f) representation to theoretical predictions for regular star polymers [2]. Still under discussion is the competition between vitrification and crystallization at higher concentrations/packing fractions. For star-like micelles no crystal formation was observed at higher functionalities, $f \gtrsim 70$, as predicted by theory. Here an amorphous gel or glass phase was found for concentrations above the overlap packing fraction η^* . At smaller functionalities, i.e. $f \lesssim 70$, 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.

We now want to relate the existence of crystalline phases in the phase diagram of star-like micelles to its exchange kinetics. It might be that the observed crystal formation is due to a structural re-arrangement of the individual micelles, which is of course prohibited for regular star polymers due to its covalent cross-linking phase.

To shed some light onto this topic, we need as a first step star-like micelles with low enough f to form a crystalline phase, but nevertheless frozen exchange kinetics. Such micelles might be formed by an “interfacial quench/jump”, i.e. by rapid changes of solvent composition. Therefore we investigated micellar re-structuring by time-resolved SANS experiments after such an “interfacial quench/jump”. Fig. 1 show the obtained SANS scattering intensities for two samples, which were independently prepared starting from the same initial solution with a mole fraction of $x_{m,d-DMF}=0.3$ and a initial polymer concentration $\Phi_{initial}=3.0\%$. One millilitre of this initial solution was rapidly poured under continuous stirring into 2ml of pure D_2O , resulting in a final solvent composition of $x_{m,d-DMF}=0.06$, and $\Phi_{final}=1.0\%$. Whereas the first sample was already prepared 9 days before the SANS beam time, the second one was mixed directly at the experiment, $\Delta t=5$ minutes for D8C8 ($\Delta t=1$ hour for the complete Q-range). As fig. 1 clearly shows, there is no difference visible. This would mean, that there is either a very fast exchange, $t \leq 5$ minutes, or no exchange at all. Fig. 1 also compares two samples directly prepared in either the initial or final solvent, now at a smaller volume fraction $\Phi=0.5\%$ to get rid of the

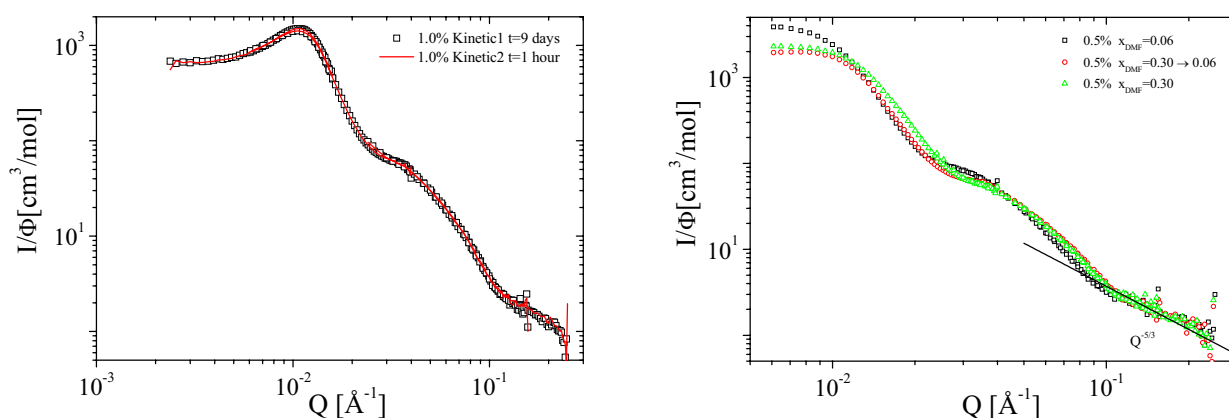


Figure 1: $I(Q)$ in absolute units vs. scattering vector Q obtained by SANS. Left hand side: Two samples after “interfacial quench/jump”. Right hand side: Samples at different solvent composition, see text

structure factor effects. Here one sees that the sample directly prepared at $x_{m,d-DMF}=0.06$ shows a bigger intensity at $Q=0$ indicating a higher functionality, whereas the forward scattering for the other two samples is more or less the same. This shows that the functionality of $x_{m,d-DMF}=0.3$ is transferred into the $x_{m,d-DMF}=0.06$ solution and that therefore the micellar exchange kinetics are still completely frozen.

References:

- [1] R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, *Macromolecules*, **37**, 9984, 2004.
- [2] R. Lund, L. Willner, J. Stellbrink, P. Lindner, and D. Richter, *Phys. Rev. Letters*, **96**, 068302, 2006.
- [3] 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:	KW1-06-014		
Experiment title:	New Hafnium based catalysts for living olefin polymerisation III		
Dates of experiment:	24.-03. – 25.03.2006	Date of report:	31.05.2006
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jörgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Juelich Institut für Festkörperforschung, Forschungszentrum Juelich Institut für Festkörperforschung, Forschungszentrum Juelich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Coates et al. [1] reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. However, the kinetics and mechanism of living olefin polymerization is still poorly understood. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization.

In recent SANS experiments we investigated the living polymerisation of poly(hexadienes) using a Titanium catalyst/MAO activator. We found that this system shows some unexpected precipitation after mixing of the individual compounds at low temperatures. I.e. rigorous stirring is required for keeping the catalyst/co-catalyst complex in solution, which is a prerequisite for successful polymerisation. Unfortunately this is not possible in the SANS cell and in particular not in the NMR cell, so that an absolute calibration in terms of sample concentration was not achievable.

Therefore we used another catalyst system to avoid this solubility problem. The new catalyst system contains a Hafnium complex as catalyst and low molecular weight Boron hydride compounds as activator. In the reactor period 2005/08 we performed first test experiments on that system and were able to follow a polymerisation in real-time by insitu-SANS. However, we discovered that the final product shows not the expected properties with respect to polydispersity and molecular weight, indicating some partially inactive catalyst/co-catalyst compounds. This would also explain the surprisingly high scattering intensity and slow kinetics observed in the scattering experiment. Meanwhile, after extensive test polymerisations, we were able to overcome these problems and follow the polymerisation under substantially improved conditions by insitu-SANS experiments.

[1] J. Tian, P. D. Hustad, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 5134.

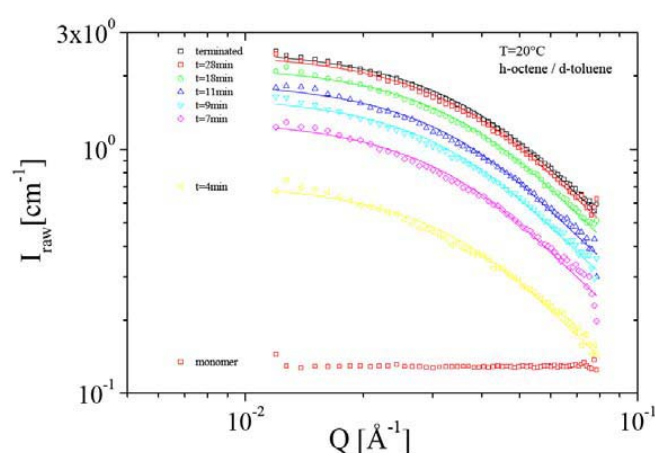


Figure 1: Living polymerisation of octene followed by real time SANS experiments at 20°C, the solid lines are fits to the Beaucage form factor.



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

Proposal number:	KW1-06-015		
Experiment title:	Exploratory study of montmorillonite nanocomposite sample preparation		
Dates of experiment:	22.03.2006 – 23.03.2006	Date of report:	17.05.2006
Experimental team: Names	Addresses		
Tobias Zacherle	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Wim Pyckhout-Hintzen	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Henrich Frielinghaus	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Wim Pyckhout-Hintzen, Dr. Henrich Frielinghaus		

Experimental report text body

In the last few years there has been a dramatic increase of research in the field of nanocomposites [1]. In particular intercalated polymers in these composites are of vital interest since they are confined in two dimensions and therefore these systems can be seen as model-systems for the conformation and dynamics of polymers in two dimensions. In the present experiment PEO and MMT were used due to their favourable interaction properties like the good adsorption of the hydrophilic PEO on the silicate surface. As the sample-preparation is somewhat tricky, we first wanted to gain some experience in it and then – in a second experiment – focus on the conformation and structure of the PEO.

The aim of this first SANS-experiment was to investigate samples obtained by different preparation processes. In general we employed two techniques which lead to even optically quite distinct samples. The first method, was to solve the PEO and the MMT in water and then to dry this solution by freezing it with fluid nitrogen and then sublimating the solvent (freeze-drying). One does obtain a fluffy material afterwards which needs to be pressed. The second method was to distillate the solution under low pressure and slowly vaporizing the solvent. This yields a gelous material which can be given onto the sample-container and further dried in the vacuum. The samples obtained by this method will be referred to as films. Four different kinds of samples were prepared:

- (1) a freeze dried sample, pressed under atmospheric pressure
- (2) a freeze dried sample, pressed under vacuum for several hours
- (3) a film
- (4) a film with oligomers added during preparation

We measured at different distances to the detector and at different temperatures T (room-temperature, 70°C, 85°C, and 100°C). We didn't find any temperature-dependence of our results. But we did find a big difference between the film and the freeze-dried-sample:

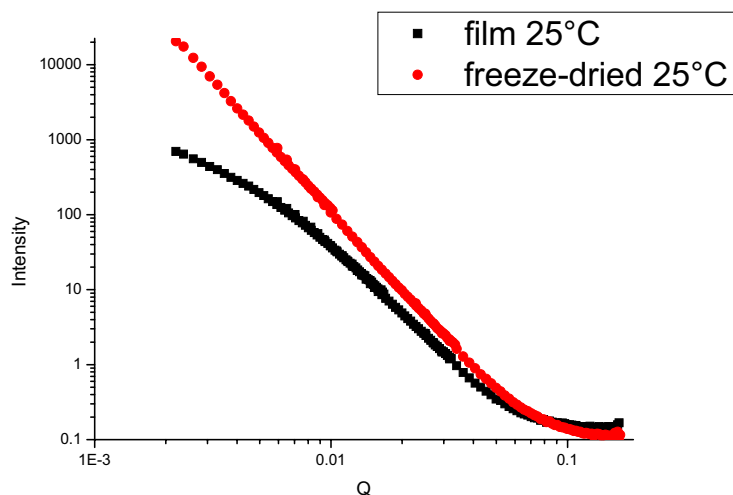


Fig1: Comparison between film and freeze-dried sample at $T = 25^\circ\text{C}$. One clearly sees less forward scattering in the film.

The film shows much less forward-scattering than the freeze-dried sample. This is believed to be due to a faulty stacking of the silicate-layers in the freeze-dried sample, which gave rise to big holes scattering at small angles because of their large sizes (with a q -dependence of q^{-4}). We didn't see any effect neither of the added oligomer nor of the different pressing procedures for the freeze-dried-sample.

The scattering-curve of the film could be fitted with the model of H. Frielinghaus [2]. In this model two Poisson-distributions of stack-sizes (tactoids) are assumed. The stacks are oriented randomly and one is able to explain the q^{-3} -dependence of the data of the film-sample.

As a conclusion one has to state, that the film-method is the best choice for the sample-preparation and we will stick to this method for upcoming experiments.

[1] R. Krishnamoorti et al.; Structure and Dynamics of Polymer-Layered Silicate Nanocomposites; *Chem. Mater.* **1996**, 8, 1728-1734

[2] H. Hermes et al.; Quantitative analysis of small angle neutron scattering data from montmorillonite dispersions; to be published in *Polymer*



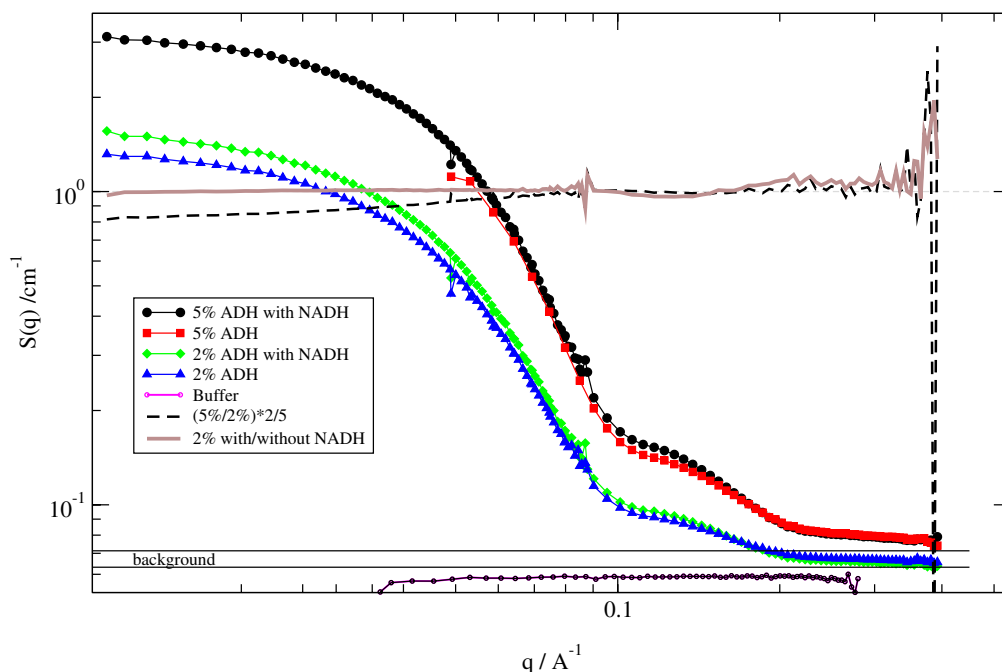
Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	KW1-06-016		
Experiment title:	Internal dynamics and structure of protein alcohol dehydrogenase by binding of cofactor: Structure		
Dates of experiment:	Apr. 2006	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:	Wim Pyckhout-Hintzen		

Experimental report text body

Most proteins are characterized by a defined tertiary structure when analyzed by crystallographic experiments. Binding of other biomolecules or substrates changes the tertiary structure of these proteins in specific regions often by more than 1 Angstrom. Intermediate states of an enzymatic reaction often depend on structural modifications. For most enzymatic reactions only a very few of these structural states are known from crystallographic snapshots since these experiments freeze the structure in a defined state. Molecular dynamic simulations as well as experiments using thermophilic proteins additionally strongly suggest highly dynamic structural fluctuations even in the absence of any bound factor. Such fluctuations are best considered as an ensemble of structural states, only some of which are competent for substrate binding or catalysis. These structural states are absolutely essential for protein function and mainly take place in protein domains also structurally modified when bound to a binding partner. The intense dynamics of specific protein regions likely adapt the protein structure to the one of its binding partner enabling its binding that would be excluded in a rigid conformation. Our experiments are directed to visualize and characterize ground state structural dynamics within a protein as well as structural fluctuations when bound to a cofactor or inhibitor. The analysis of proteins either bound or unbound to additional factors will allow the detailed characterization of dynamic protein areas and may possibly open a new way in protein dynamic analysis. Up to now a direct experimental observation of such protein dynamics is still missing.

As model system we depend on a protein with known structural transformations upon substrate binding. These transformations may be on the large or small scale between protein domains of sufficient size. Here, the alcohol dehydrogenase (ADH) from yeast will be used as model system. In our Experiment we want to examine configurationally changes due to binding of the cofactor to assist our planned experiments by neutron spin echo spectroscopy.

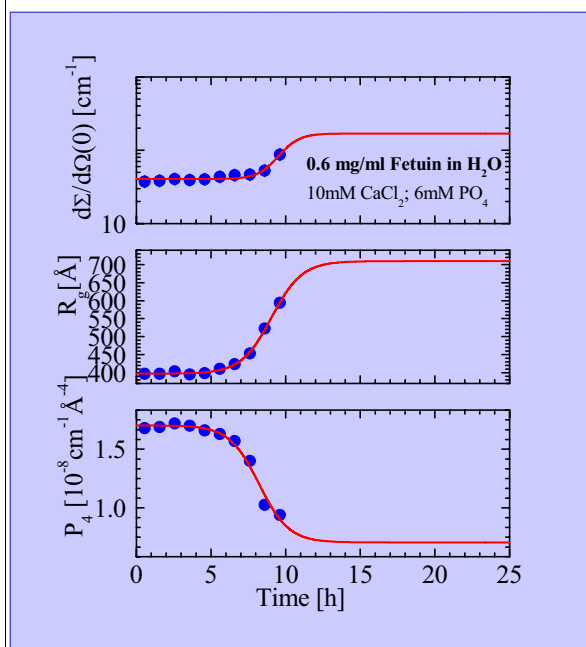


The graph shows the SANS data for concentrations of 2% and 5% with and without added NAD. The low q part of the 5% without NAD is missing due to a frozen sample. The shoulder above $0.1 \text{ \AA}^{-1}$ is typical for the tetrameric flat structure (two dimers parallel oriented) as it isn't found for the dimeric structure. The expected small peak at about $0.3 \text{ \AA}^{-1}$ was not detected as it is smeared by the resolution of the instrument and results only in a small plateau. To compare the structural features we calculate, after subtracting the flat background, the ratio between the 2% curves and between the 2 concentrations with added NAD. For the 2% samples we observe over the full range of accessible scattering vectors a flat structure less curve. An additional constant factor of 0.86 accounts for the obvious loss of concentration between the two curves. Compared to the 5% sample we observe a decrease of intensity at low q . This is due to an increasing interaction between the proteins as they are closer at this higher concentration. We observe the influence of the structure factor. From these data we can only conclude that the effect of a bound NAD is less than we can detect with these measurements.

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

Proposal number:	KW1-06-017		
Experiment title:	SANS Untersuchung zur Stabilitätsgrenze kolloidaler Protein-Mineral Aggregate		
Dates of experiment:	07.04-12.04.2006	Dates of report:	02.06.2006
Experimental team: Names	Addresses		
Dr. Wolf-Alexander Heiß	IZKF BioMAT Universitätsklinikum Pauwelsstraße 30 D-52074 Aachen		
Dietmar Schwahn Hitoshi Endo	IFF, FZ-Jülich, D-52425 Jülich		
Local Contact:	Dietmar Schwahn		

Experimental report text body



Fetuin-A in a supersaturated solution with regard to calcium and phosphate produces colloidal protein – mineral particles, denoted as CPPs. Preliminary investigations with our biochemical precipitation assay concerning the limits of CPP stability evidenced that at least 0.6 mg/ml fetuin-A are necessary to stabilize a solution containing 10 mM CaCl_2 and 6mM PO_4 at pH 7.4.

In this series of experiments we observed an increase in scattering intensity after roughly 8h at room temperature. At the same time the radius of gyration increased starting from 400 $\text{\AA}$ while the total surface extension decreased.

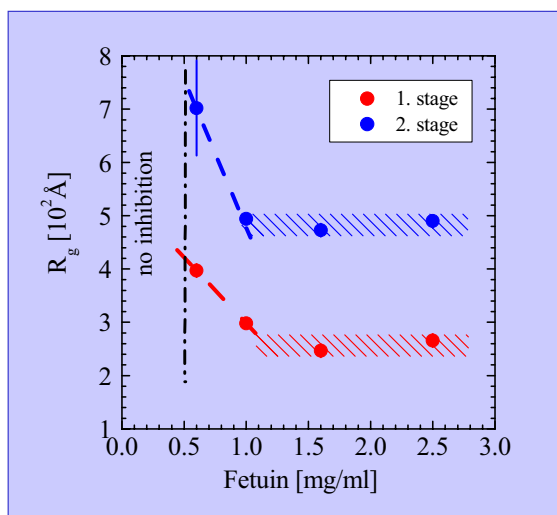


Figure 2 shows the relationship between the fetuin-A concentration and the radius of gyration at our standard supersaturation (10 mM CaCl₂, 6 mM PO₄). At high fetuin-A concentrations (>1.2 mg/ml) small CPPs with a radius of gyration of approximately 250 Å formed for the first ripening stage and of approximately 500 Å for the second, respectively. A reduction below that threshold of 1,2 mg/ml fetuin-A led to considerably larger CPPs with a radius of gyration of 300 – 400 Å for the first stage and max 700 Å for the second, respectively. Moreover, these experiments confirmed our results obtained from our precipitation assay that 0.5 -0.6 mg/ml fetuin-A represent the lower limit of CPP

stability.



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

Proposal number:	KW1-06-019		
Experiment title:	New Hafnium based catalysts for living olefin polymerisation IV: Effect of reaction temperature.		
Dates of experiment:	20.04.2006	Date of report:	01.06.2006
Experimental team: Names	Addresses		
Aizhen, Niu Jörg, Stellbrink Jürgen, Allgaier	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Pyckhout-Hintzen, Wim		

Experimental report text body

Coates et al. [1] reported a new stereoselective titanium complex for olefin polymerization. Upon treatment with methylaluminoxane (MAO), this complex was found to be active for the polymerization of propylene at 0°C in toluene. Unexpectedly the obtained polymer exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$). The amazing point is that the first synthesis of high molar mass syndio-polypropylene-block-poly(ethylene-co-propylene) diblock copolymer ($M_n = 145\,100$, $M_w/M_n = 1.12$) was achieved, when a slight overpressure of ethylene was added to the reactor after formation of the living syndiotactic polypropylene. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler-Natta catalysts. However, the kinetics and mechanism of living olefin polymerization is still poorly understood. On the basis of research experience and knowledge of living anionic polymerization of dienes and styrene, we plan to develop the combined time resolved NMR and SANS technique to the field of living olefin polymerization, discover the fundamental mechanism and kinetics of the living olefin polymerization. In recent SANS experiments we investigated the living polymerisation of poly(octene) using a new catalyst system contains a Hafnium complex as catalyst and low molecular weight Boron hydride compounds as activator. In the reactor period 2005/08 we performed first test experiments on that system and were able to follow a polymerisation in real-time by insitu-SANS. However, we discovered that the final product shows not the expected properties with respect to polydispersity and molecular weight, indicating some partially inactive catalyst/co-catalyst compounds. This would also explain the surprisingly high scattering intensity and slow kinetics observed in the scattering experiment. Meanwhile, after extensive test polymerisations, we were able to overcome these problems and followed the polymerisation under substantially improved conditions by insitu-SANS experiments. Now the expected molecular weight is finally obtained and the polymerisation

could be followed although the kinetics are extremely fast (The polymerisation is already completed after approximately 30 minutes: Analysis of the forward scattering $I(Q=0)$ as a function of time gives a characteristic time of only 8.3 minutes at 20°C). Another clear result is that the growing chain is not aggregated as we know for “living” anionic polymerisation [2-4], because the polymerizing chain at full conversion shows the same scattering profile as the terminated chain.

To follow the structural changes in more detail we planed to decrease temperature to about 0°C to slow down the polymerisation. Unfortunately, the catalyst of this reaction has only 50% activity, we have to wait for the preparing of a new catalyst. Therefore the final product from last experiment on KWS1 was characterized at different concentrations. Further data analysis and corresponding NMR measurements are in progress.

[1] J. Tian, P. D. Hustad, G. W. Coates, *J. Am. Chem. Soc.*, **123**, 5134 (2001).

[2] A.Z. Niu, J. Stellbrink, J. Allgaier, L. Willner, A. Radulescu, D. Richter, B.W. König, R.P. May, L.J. Fetters, *J. Chem. Phys.*, **122**, 134906 (2005).

[3] J. Stellbrink, J. Allgaier, L. Willner, D. Richter, T. Slawecki, L.J. Fetters, *Polymer*, **43**, 7101, (2002)

[4] J. Stellbrink, L. Willner, O. Jucknischke, D. Richter, P. Lindner, L.J. Fetters, J.S. Huang, *Macromolecules*; **31**, 4189 (1998) and *Macromolecules*, **32**, 5321 (1999).



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

Proposal number:	KW1-06-020		
Experiment title:	Comparison of stretched PS melts: influence of architecture		
Dates of experiment:	13.04. – 16.04.2006	Date of report:	14.05.06
Experimental team: Names	Addresses		
Pyckhout-Hintzen, W. Jens Kroman Nielsen	FZJ DTK Copenhagen		
Local Contact:	Wim Pyckhout-Hintzen		

Experimental report text body

We had proposed to measure the strain and tube diameter in deformed polystyrene melts which are partially labelled and/or vary in the architecture.

Recent developments in the description of the scattering patterns of deformed melts have lead to new discussions. A major topic of this is the size of the tube diameter which comes out of small angle neutron scattering data, neutron spin echo spectroscopy and last but not least from linear rheology.

The previous success in describing the relaxation of a linear polyisoprene as a function of time after a step strain has opened the door to different architectures which, depending on the labelling, should be more or less active towards relaxation. 3 different blends which separately from each other have been evaluated at different times and with different prognostics about what is going to be the main parameter of determination for the anisotropy could reveal new information and sustain the former observations. A model-independent technique as e.g. neutrons spin echo is still necessary, however.

The proposal has been combined with a former KW1 proposal on deformed rings (KW1-05-061) and deformed diluted PS-triblocks (KW1-05-62) and data from these will be just transferred. The new data concern mainly the linear homopolymer blend which was actually present in both former experiments.

$S(q)$ can be written as

$$S(q) = \frac{1}{N^2} \sum_{i,j} \exp(-q^2 \langle r_{ij}^2 \rangle / 6)$$

which can be written of course in its single components x, y and z. That means that the scattering law is only determined by the mean square distance between pairs of monomers.

The scattering now sees 2 things: first, there is a time-average which one can write as

$$r = \bar{r} + \delta r$$

and the ensemble average which then can be written as

$$\langle r^2 \rangle = \langle \bar{r}^2 \rangle + \langle (\delta r)^2 \rangle$$

and δr is the instantaneous fluctuation away from a mean position.

The mean position of a polymer chain is of course determined by the environment which can be network or crosslinks or just the fact that there are other chains. The chain axis couples affinely to the macroscopic deformation and therefore we could write $r \rightarrow \lambda r$ and

$$r = \lambda \bar{r} + \delta r$$

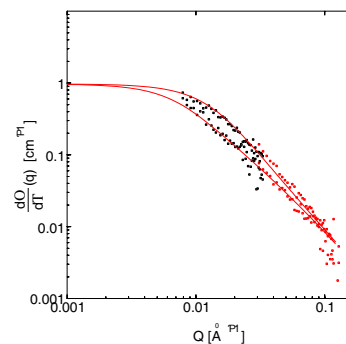
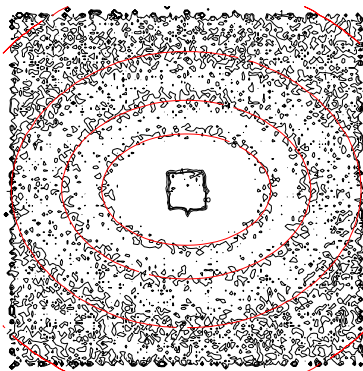
The fluctuations are treated as harmonic potentials and one can assume all kinds of deformation couplings to the strain. E.g. for networks it was found by several authors that the fluctuation width couples to the strain with $\sqrt{\lambda}$ whereas for uncross linked chains typically no deformation dependence could be found experimentally. We will stick to this last observation.

This means also inherently that the total deformation of a chain is always somewhat less than affine. Therefore the difference between the chain's deformation at the smallest angles and the deformation in a spatial range which corresponds to the fluctuation width is measurable with SANS.

This problem has been solved for a constrained cross linked linear chain inside a phantom network or melt and discussed by Warner and Edwards 1982. The scattering theory for a tube-constrained linear chain has been worked out by us (and afterwards confirmed by Read et al) and leads to the structure factor

$$S(q, \lambda) = 2 \int_0^1 d\eta \int_0^\eta \prod_{x,y,z} \exp(-(qR_g \lambda)^2 (\eta - \eta') - (qR_g)^2 (1 - \lambda^2) \left\{ \frac{d^2}{2\sqrt{6}R_g^2} (1 - \exp(-\frac{(\eta - \eta')}{d^2})) \right\} \frac{d^2}{2\sqrt{6}R_g^2})$$

Fits to a deformed sample were successful and yield ideal values for $R_g = 147.5 \text{ \AA}$ which agrees with the estimate of $R_g = 0.28 \sqrt{Mw}$ and a tube radius of about $(47.0 \pm 5) \text{ \AA}$, i.e. $(94 \pm 5) \text{ \AA}$ tube diameter. This is in perfect agreement with data from the plateau modulus and agrees also well with the segmental fluctuation range, i.e. about $80 \text{ \AA}$ of the PS rings at a comparable deformation. The tube radius is not deformed as was the case for linear poly-isoprene. Further comparison has still to be done.





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

Proposal number:	KW1-06-021		
Experiment title:	Study of montmorillonite nanocomposite structure and comparison to previous results		
Dates of experiment:	13.04.2006 – 14.04.2006	Date of report:	17.05.2006
Experimental team: Names	Addresses		
Tobias Zacherle	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Wim Pyckhout-Hintzen	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Henrich Frielinghaus	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Wim Pyckhout-Hintzen, Dr. Henrich Frielinghaus		

Experimental report text body

Polymer-clay-composites are of big interest due to the fact that they represent model-systems for polymers confined in two dimensions [1]. In addition to that there is a wide range of possible applications of these new materials [2]. The material under investigation in this experiment was a PEO-MMT-composite. Since we had compared the different kinds of preparation-methods in a previous experiment and had found the film-preparation to be the best choice, all the samples used in the experiment were films. Further on we used D_2O as solvent during preparation, because of its superior scattering properties compared to ordinary water.

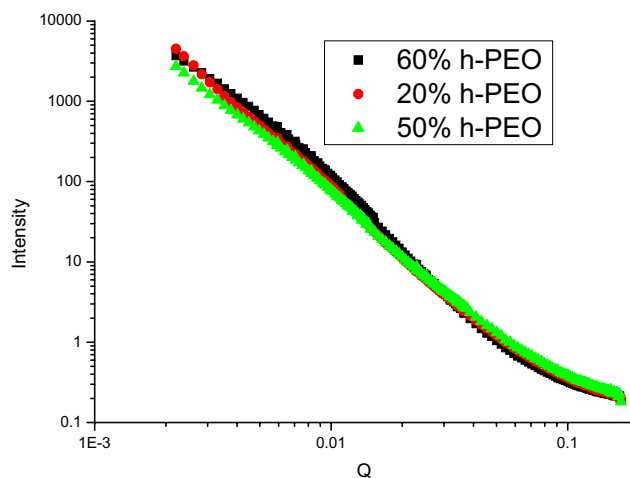
In the present experiment, we tried a contrast-match between the silicate layers and the PEO. Therefore we made a blend of deuterated and protonated PEO in order to match the average scattering length of the polymer with the one of the MMT. In this way we hoped to eliminate the scattering of the silicate stacks and to obtain a pure polymer-signal. By analyzing this signal one can conclude the radius of gyration of the polymer confined in between the silicate layers and thus see the conformation of the PEO in two dimensions.

We did prepare 3 samples with different relative content of deuterated-protonated PEO, whereas the total amount of PEO remained fixed: 20 weight-% PEO, 80weight-% MMT:

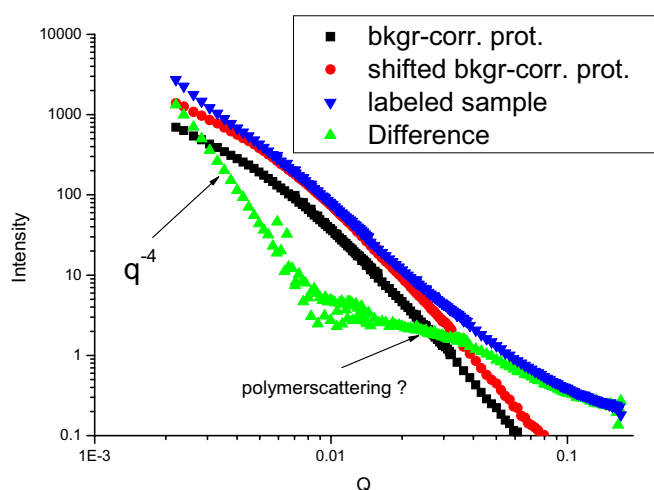
- (1) 50 vol-% protonated PEO
- (2) 20 vol-% protonated PEO
- (3) 60 vol-% protonated PEO

The expected matching point was for 50 vol-% protonated PEO. Typical adsorption-times of the PEO in the literature are 24 h (although this is unknown), so the two polymers were added successively.

Our results are presented below:



One sees that „stack-scattering“ is still dominating, as there is no hint of a Guinier-plateau, which would be an indication of the wanted polymer-scattering. So we did not succeed with our contrast-match. Although the theoretical matching condition shows smaller excess-intensity and a more polymer-like q-dependence at low q.



A preliminary analysis under the assumption of additivity of scattering contributions of polymer and silicate reveals two features:

- 1) We might have had phase-separation of the deuterated and protonated PEO. This is indicated by the green line. The exponent of the q-dependence at low q can be explained by large regions having contrast in scattering-length, which would occur if the two kinds of PEO had not mixed.
- 2) We saw polymer-scattering in the form of a Debye-curve at higher q, but it cannot be excluded that this signal comes from PEO, which was not intercalated between the silicate platelets.

Possibly a preferential adsorption of one of the polymers due to the successive addition has hampered the contrast-match-conditions. Adsorption-time is apparently much shorter than 24 h.

For the experiments in the future we will improve our sample-preparation-process in order to avoid phase-separation and finally get the desired contrast-match.

[1] R. Krishnamoorti et al.; Structure and Dynamics of Polymer-Layered Silicate Nanocomposites; *Chem. Mater.* **1996**, 8, 1728-1734

[2] S. S. Ray, M. Okamoto; Polymer/layered silicate nanocomposites: a review from preparation to processing; *Prog. Polm. Sci.* **2003**, 28, 1539-1541