

Focusing-Mirror High-Resolution Small Angle Scattering Instrument and Reflectometer (KWS-3)



Instrument Parameters

Wavelength:	$\lambda = (12.7 \pm 0.6) \text{ \AA} \text{ (9\% FWHM)}$
Entrance aperture:	$r_E = 1 \text{ to } 10 \text{ mm}$
Wave vector resolution given by the opening of the entrance aperture:	$\Delta Q = k r_E / L \quad (k = 2\pi/\lambda)$
Scattering wave vector range:	$10^{-4} \leq Q \leq 2 \times 10^{-3} \text{ \AA}^{-1}$ $10^{-4} \leq Q_z \leq 0.08 \text{ \AA}^{-1}$ in reflectometry mode
Neutron intensity at sample position is proportional to the surface of the entrance aperture:	$I = 180 \text{ n/s per mm}^2$ entrance aperture; for a wave vector resolution of $10^{-4} \text{ \AA}^{-1}$ ($2 \times 2 \text{ mm}^2$ entrance slit aperture) the intensity is therefore 720 n/s
Cross section of beam at sample position:	10 cm wide, 2 cm high
Detector:	Position sensitive detector, 8 cm diameter, $1.5 \times 1.5 \text{ mm}$ resolution

Instrument Responsible

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

Proposal number:	KW3-04-008, KW3-04-015		
Experiment title:	Influence of solvent quality on the micellization behaviour of PEP-PEO		
Dates of experiment:	6.-15. 10. 2004 24.-26. 8. 2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
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Local Contact:	J. Stellbrink		

Experimental report text body

Very recently we started using giant, star-like micelles (PEP5-PEO120, the number denotes the molecular weight in kg/mol) [1] as “*tunable analogs*” of unimolecular, regular star polymers. Here we found, that the intensity profile obtained for a micellar solution in a solvent mixture with a mole fraction $x_{\text{DMF}}=0.5$ shows completely different features than those for other mixtures. Whereas for solvent compositions $x_{\text{DMF}}=0, 0.1, 0.2, 0.3$, and 1 we found an intensity profile typical for a concentrated solution of micelles, *i.e.* a strong structure factor peak followed by an extended power law decay due to the blob scattering of the corona, the scattering profile for $x_{\text{DMF}}=0.5$ is dominated over nearly the whole Q-range, including that of the U-SANS instrument KWS-3, by a sequence of power laws. This is probably a precursor of the demixing of the micellar solution at this DMF mole fraction, which is found to take place at $T \approx 25^\circ\text{C}$ (The solution gets turbid) [2,3]. We have to emphasize that at the investigated temperature, $T \approx 30^\circ\text{C}$, the micellar solution is macroscopically completely clear and homogeneous.

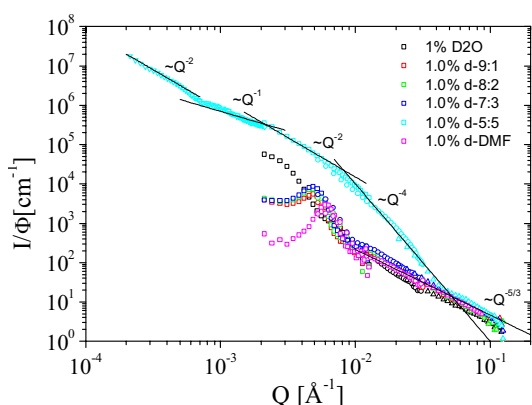


Figure 1: Intensity profile obtained by a combined U-SANS/SANS experiment vs. scattering vector Q for PEP5-PEO120 micelles in different mixtures of water and DMF.

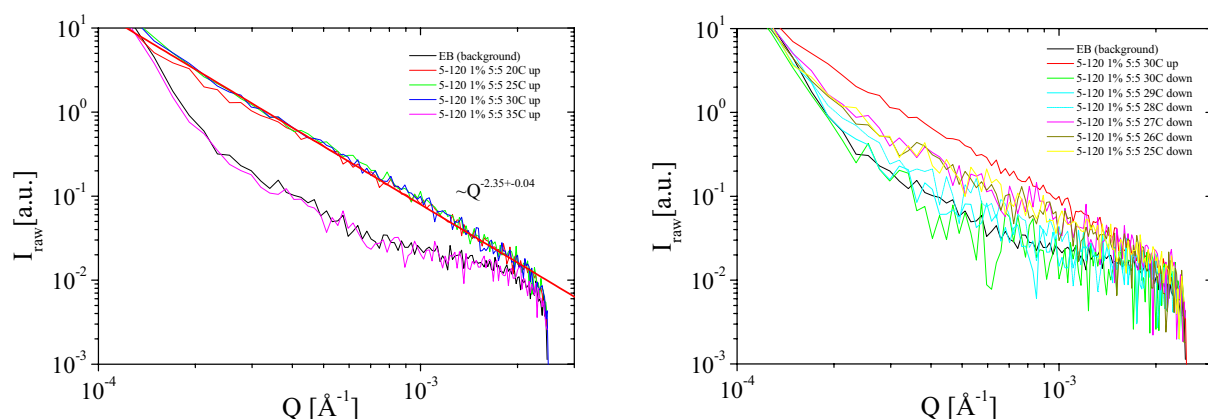


Figure 2: Intensity vs. scattering vector Q as a function of temperature upon heating (left) and cooling (right) for a micellar solution of PEP5-PEO120 in a water/DMF mixture with mole fraction $x_{m, dmf}=0.5$.

In this experiment we investigated in more detail the temperature effects in the U-SANS Q -range covered by KWS-3, i.e. $2 \times 10^{-4} \leq Q \leq 2 \times 10^{-3} \text{ \AA}^{-1}$. We found that the observed scattering curves depend crucially on thermal history of the sample, as can be seen in fig. 2. Here raw data for a temperature series upon heating (left) and cooling (right) are shown in comparison with the empty beam profile as background. Starting from the completely demixed state we slowly increased the temperature to 30°C and kept it constant for 12 hours, but still the typical power law $I \sim Q^{-2.35}$ of the demixed state is found. Only if the sample is heated further up to 35°C the intensity quickly decreases until it finally reaches the background level. Upon cooling down again to 30°C , the intensity is not increasing again, even if the sample is kept at 30°C for several hours. Only after further cooling down to 27 - 26°C the previously observed power law slowly appears again. This means that the phase separation kinetics are extremely slow, which might results from the special need to form micelles (upon heating) and to dissolve these micelles (upon cooling), respectively during this phase transition. A phenomenon which certainly needs further investigation.

References:

- [1] L. Willner, A. Poppe, J. Allgaier, M. Monkenbusch, D. Richter, *Europhys. Lett.*, **55**, 667 (2001)
- [2] R. Lund, L. Willner, J. Stellbrink, A. Radulescu and D. Richter, *Macromolecules*, **37**, 9984, 2004.
- [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:	KW3-04-014		
Experiment title:	Structure analysis of sintered tungsten wires by SANS		
Dates of experiment:	23.01. – 30.01.2005	Date of report:	24. 05. 2006
Experimental team: Names	Addresses		
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Experimental report text body

Tungsten wire is the most frequently used material for lighting, electronic devices, thermocouples, cathodes. The usual temperature range in most of such wire applications needs extremely good high-temperature mechanical properties, e.g. good creep-resistance, high tensile-strength, resistance to early deformation and vibration. The doped tungsten ful-fills these requirements. During the sintering most impurities escape, except a part of potassium, which remains in bubbles during the following thermomechanical treatments and the whole life of the lamp. The presence of potassium filled bubbles with characteristic diameter of 100 nm is responsible for the quality of the wire. The structure of bubbles follows the macroscopic deformation of the wire. As a consequence of oriented macroscopic strain induced by wire drawing the bubbles are oriented parallel to the wire axis. To analyse the morphology of the wires in the whole volume of the sample, we used the method of neutron scattering. Previous SANS measurements on samples taken from different steps of annealing were made. To analyse the relative surface changes of different shaped potassium bubbles a simple way of data treatment was used. We have found that even at the highest studied annealing temperatures a substantial amount of elongated inclusions remain in the wires. The present USANS measurement objective was to obtain information in ultra-small q range. The measurements were carried out on the KWS-3 USANS instrument. The measured samples were: unannealed; annealed at 1150°C; annealed at 1850°C; annealed at 2200°C. The sample - detector distance was 9.3 m; the wavelength: 12.7 Å. These samples were taken from the different steps of heat treatment. The 0.5 mm diameter tungsten wires were placed in 3 layers in the aluminium sample holder.

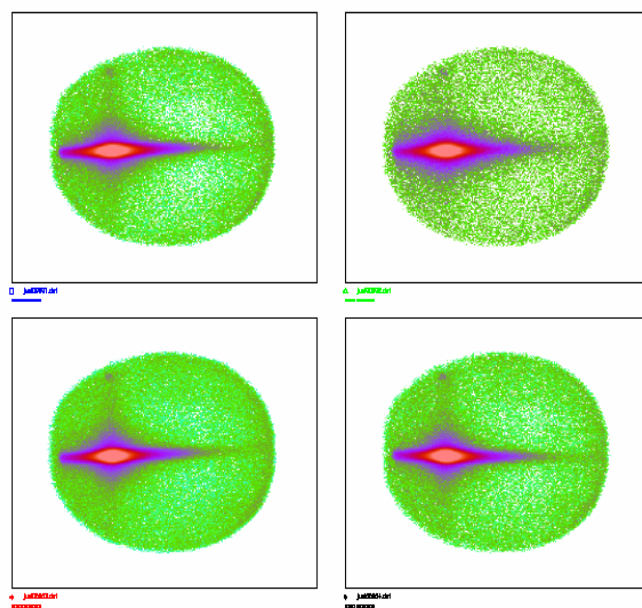


Fig.1. 2D scattering maps of the measured tungsten wires

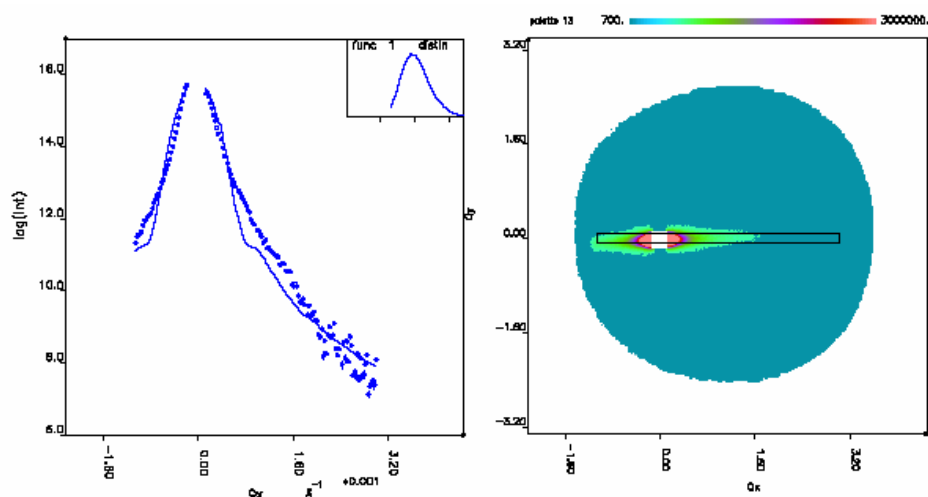


Fig.2. 2D fit of the unannealed tungsten sample

A rough two dimensional data treatment was made by using the cylinder model, which in comparison to the previously used model of ellipsoid proved to be a better approximation of the nano-scale structure of the tungsten wires. The low q range allowed us to obtain information about the size of the most elongated potassium filled bubbles.



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

Proposal number:	KW3-04-016, DKD-04-005		
Experiment title:	The large-scale structures and morphologies formed by the co-crystallization of PEB-n random copolymers and paraffin waxes (5)		
Dates of experiment:	9.09.2004 – 24.09.2004 11.03.2005 – 15.03.2005 19.04.2005 – 22.04.2005 19.05.2005 – 23.05.2005	Date of report:	29.05.2006
Experimental team: Names	Addresses		
Aurel Radulescu, Emmanuel Kentzinger, Jörg Stellbrink, Dietmar Schwahn, Manfred Heiderich	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
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Experimental report text body

As conventional SANS revealed [1,2] the PEB-n random copolymers form in solution needle-like aggregates in decreasing temperature. When paraffin wax is added to the polymer solution the scattering patterns collected under different contrast conditions and revealing the conformation of the polymer or wax within the common aggregates change strongly in comparison with the case of single polymer or paraffin wax solutions. When the copolymer self-assembles at temperatures higher than the wax crystallization point a complex shish-kebab-like morphology seems to occur [2]. Formation and structural evolution of such morphology was only partially understood by analysing the conventional SANS data. These allowed only an incomplete characterization of the common polymer-wax aggregates which seem to extend rather vastly in size surpassing the length scale covered by the conventional SANS method. Therefore new structural investigations were performed by involving the focusing-SANS (F-SANS) and the ultra- SANS (U-SANS) instruments set-up at the FRJ-2 reactor in Jülich. Combining the conventional-, focusing- and ultra-small angle neutron scattering methods the multilevel structures showing characteristic sizes from 10 μm to 1 nm and formed upon cooling in common solutions of semi-crystalline PEB-7.5 copolymers and waxes could be fully characterized. The conformation of the polymer and wax molecules within the common aggregates was analysed separately by using the contrast matching. The structural and density parameters of the aggregates have been evaluated using models. The experimental data collected in a slit-geometry at the U-SANS double-diffractometer were transformed into the pin-hole geometry according to a procedure described in [3]. An example of the scattering data collected over a very wide Q-range is given in Fig.1 where the scattering patterns under wax contrast are present at two temperatures within the wax-copolymer common aggregation regime for a mixed solution of 0.6% low M_w PEB-7.5 copolymer and 4% C_{24} wax in decane. The Q^{-2} power law behaviour at intermediate Q and the peak at around $Q^*=0.025 \text{ \AA}^{-1}$ shown at 0°C (also by the polymer scattering patterns not presented here) reveal a co-crystallization of polymer and wax into thin, very large platelets forming a correlated arrangement.

The lateral size of these platelets can be evaluated by analysing the Guinier regime identified at low Q . The model analysis of this morphology in terms of the paracrystalline structure factor applied to an ensemble of finite size discs, each disc being made by a wax and a polymer embedded layers is presented as solid line. The wax scattering pattern at -10°C reveals that the wax massively crystallizes and grows from thin platelets into large objects with sharp interfaces (Q^{-4} power law at higher Q). From an inspection of the low Q data measured by FSANS (10^{-4} to $2 \times 10^{-3} \text{ \AA}^{-1}$) and USANS (below $10^{-4} \text{ \AA}^{-1}$) a coexistence of two structures showing different characteristic sizes can be identified (the vertical arrows indicate the observed Guinier regimes). The smaller shows a 2-dimensional morphology that is revealed by the Q^{-2} power law regime identified within the Q range covered by FSANS. The unified Beaucage equation [4] for multiple structural levels and scattering data extending over many decades describes well the F-SANS data and prove the existence of thick plates ($d=0.23 \mu\text{m}$) which must result by the filling of the space between the thin correlated platelets identified at 0°C with continuously growing wax crystallites. The additional scattering at low Q indicates the formation of much larger aggregates whose characterization is difficult. This is done by analysing scattering data where the Guinier regime is absent. A 1-dimensional morphology can be tentatively attributed to these aggregates via the assignment of Q^{-1} for low Q . The neutron scattering findings for this later aggregation stage were complimented by the microscopy observations shown in Fig.2. Different copolymer-wax combinations and wax amounts investigated for the case of the copolymer self-assembling event occurring well-before the wax crystallization point revealed basically the same common crystallization features as those described above and thus, the formation and evolution of a hierarchical morphology showing multilevel structures. First, the polymer 1-dimensional morphology showing density modulations occurs [1]. Then, wax crystals are formed and nucleated by the crystalline nuclei of the polymer needles. The wax grows laterally in large platelets also involving further polymers still in solution. The primordial polymeric structure serves to template the lateral platelets in a correlated shish-kebab-like arrangement. Late aggregation leads to a massive crystallization of the wax surplus and formation of large compact 1-dimensional structure.

References: [1] H.S.Asbaugh et al., *Macromolecules* 35, 7044, 2002; [2] A.Radulescu et al., *J.Pol.Sci. B* 42, 3113, 2004; [3] D.Schwahn, and M.H.Yoo, *Springer Proceedings in Physics* vol.10, Springer Verlag: Berlin, Heidelberg, New York, Tokyo, 1986, p 83; [4] G.Beaucage, *J.Appl.Cryst.* 29, 134, 1996.

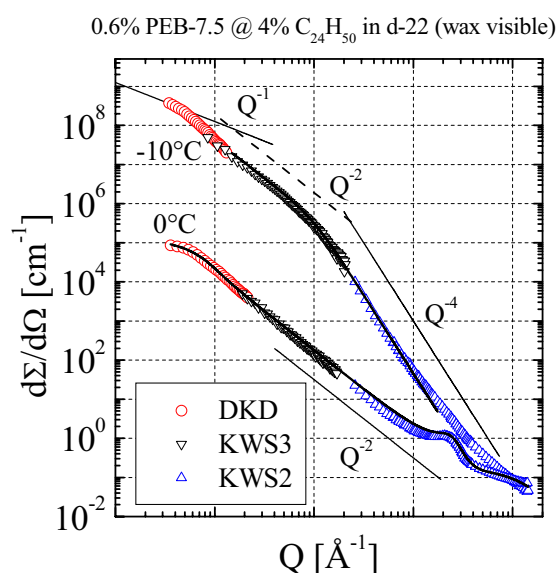


Fig.1 - Scattering patterns under wax contrast from a mixed solution of 0.6% low M_w PEB-7.5 copolymer and 4% C_{24} wax in decane.

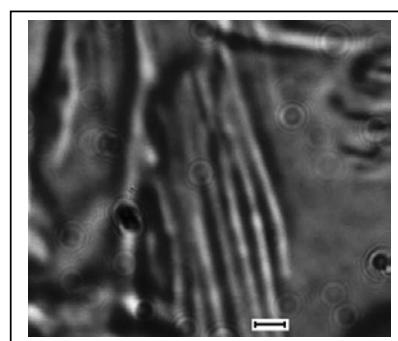


Fig.2 – A micrograph of the aggregates formed in the same solution at -10°C (scale bar $10 \mu\text{m}$).



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

Proposal number:	KW3-05-004		
Experiment title:	Fractal geometry study on different polymerization stage of Ziegler-Natta $\text{MgCl}_2/\text{TiCl}_4$ /polypropylene system by small angle neutron scattering		
Dates of experiment:	2005-9-29	Date of report:	2005-12-20
Experimental team: Names	Addresses		
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Chen, Dongfeng			
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Experimental report text body

Since the Ziegler-Natta catalyst was discovered in the laboratories of K. Ziegler in the fall of 1953 and G. Natta in spring of 1954 it is commercially very important and deserves the attention of the scientific and engineering community. So the growth of the polymer particle has aroused much interest in both academic and industrial laboratories [1-3]. This kind of molecules has been studied in the past years using a variety of techniques such as light microscopy, electron scanning microscopy, atomic force microscopy and optical tweezers yielding information on the shape, dynamics and mechanical properties [4]. However, these techniques require samples to be tethered to surfaces which could change the real shape of the polymer. The understanding and the full control achieved on the catalyst “replication” phenomenon have given a real “new dimension” by fractal geometry [5-7]. With the aid of concepts in fractal geometry, the relevant aspects of the structure of polypropylene based on Ziegler-Natta supported catalysts can be derived from small angle neutron scattering (SANS) experiments. The purpose of the SANS measurements performed on KWS-1 and KWS-3 was to get the fractal information on Ziegler-Natta $\text{MgCl}_2/\text{TiCl}_4$ /polypropylene system.

In this experiment, we investigated the effects of polymerization time. To get different shape we choose two of them polymerized in high pressure and the last one polymerized in normal pressure. The polymerization time of the two samples polymerized in high pressure is half an hour and one and a half hour respectively, named as the medium sample and the big sample according to their sizes of the particles. The polymerization time of the last one polymerized in normal pressure is half an hour named the small sample. All the other conditions are the same among the three samples. One part of the experiment was carried out on KWS-1. for Q values ranging from $2.0 \times 10^{-3} \text{ \AA}^{-1}$ to $1.5 \times 10^{-1} \text{ \AA}^{-1}$. The other part of the experiment was carried out on KWS-3. for Q values ranging from $2.2 \times 10^{-5} \text{ \AA}^{-1}$ to $2.7 \times 10^{-3} \text{ \AA}^{-1}$. The data was gotten at room temperature with air in these three samples.

From Fig.1 we can see the scattering from the three samples shows a Q^{-4} power-law behavior which leads to the conclusion that from the scattering data we only can see a porous mass fractal due to the interaction between the particles and the air.

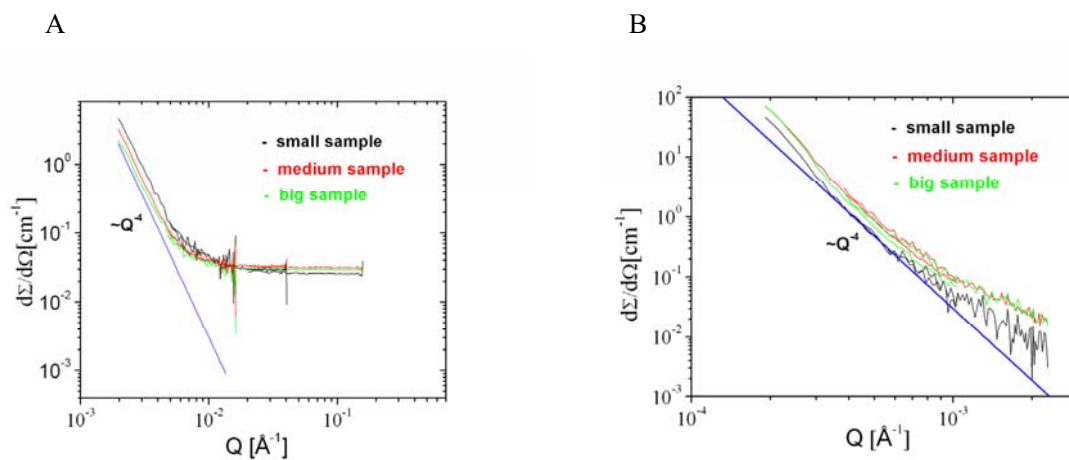


Fig. 1 Scattering pattern from PP measured at room temperature by using (A) KWS1 (B) KWS3 spectrometers in jülich. The power law regimes are indicated.

The interaction between the particles and the air is so strong that we can't get the other fractal information we really need from the experiments. So in future experiments we will measure with the sample solved in some kind of deuterated solvent in order to avoid this interaction to get the information of fractal geometry under consideration.

References

1. Ziegler, K., Angew. Chem., 1952, 64, 323.
2. Natta, G., Pasquon L., and Giachetti, E., Angew. Chem., 1957, 69, 213.
3. Natta, G., J. Polym. Sci., 1955, 16, 143.
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5. Mandelbrot, B. B., The Fractal Geometry of Nature, Freeman Press, San Francisco, 1982
6. McCarthy, D. W., Mark, J. E., Schaefer, D. W., Journal of Polymer Science: Part B: Polymer Physics, 1998, 36, 1167
7. Schaefer, D. W., Science, 1989, 243, 1023



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

Proposal number:	KW3-06-001		
Experiment title:	Wax conformation within the large-scale morphologies in mixed solution of PEB-n copolymers and paraffin waxes		
Dates of experiment:	11.03.06-14.03.06	Date of report:	06.06.2006
Experimental team: Names	Addresses		
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Local Contact:	Dr.E.Kentzinger		

Experimental report text body

The self-assembly of poly(co-olefins) in dilute solution has been shown via SANS to yield either plate-like or needle-like micelles-like micelles [1,2]. The resultant supramolecular structures are dependent upon the copolymer architecture. The crystalline-amorphous diblock co-polymers yield self-assembled hairy plates while the corresponding random co-polymers yield one-dimensional needle shaped aggregates. The PEB-n random copolymers (n - the number of ethyl sides per 100 backbone carbons) show selectivity in their wax crystal modification capacities depending on the ethylene content of the backbone. This behavior relates to the graded ethylene content of PEB-n copolymers that leads to different self-assembling temperatures: the lower n, the higher the self-assembling temperature [2]. All PEB-n copolymers self-assemble in open 1-d structures. This conclusion has stimulated further structural studies of multiblock copolymers in solution where blocks represent poly(ethylene-butene) random copolymers (PEB-n) showing graded ethylene contents and thus, different crystallization degrees. Recently [3] conventional and focusing SANS studies of self-assembling in decane solution of a triblock and tetrablock PEB-n copolymers have been performed. The structural results complimented by microscopy observations concluded that these materials form in solution core-shell structures showing a 1D overall aspect which associate and give raise to occurrence of large scale spherulitic-like soft aggregates with sizes within the micrometric range. The conventional SANS investigations have shown that these multiblock copolymers modify the wax crystals morphology from big compact crystals with sizes of hundreds of micrometers as in the case of pure wax solution into 2-dimensional thin aggregates. In the present study we investigated at the focusing SANS KWS3 instrument several mixed solutions of paraffin waxes and multiblock copolymers in order to obtain first information about the wax conformation at larger scale within the common wax-copolymer aggregates. An example of raw scattering patterns collected at room temperature from a mixed solution of C36 wax and tetrablock PEB-2.6/6.0/10.9/13.2 copolymer is shown in Fig.1. Unfortunately, the copolymers were available only in protonated state therefore, for allowing the wax visible we were forced

to use highly protonated solvent in order to match it with the polymer. This led to a strong multiple scattering effect which can be identified by the very low level of the samples forward scattering in comparison with that of the empty beam. Accordingly, the samples transmission is very low. Nevertheless, qualitative information about the wax morphology can be obtained which are expected to be useful for a more complete view of the structure and morphology of the common wax-copolymer aggregates in a combination with the conventional SANS data.

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

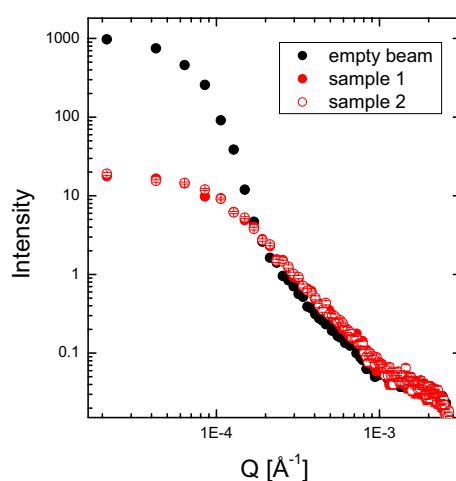


Fig.1 – The scattering intensities of two wax-copolymer mixed solutions in decane for C36 and PEB-2.6/6.0/10.9/13.2 tetrablock in parallel with the empty beam measurement.



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

Proposal number:	KW3-06-002		
Experiment title:	Measurement of two reference samples in the framework of the benchmarking of the SANS instruments of the HGF		
Dates of experiment:	20.03. - 22.03.2006	Date of report:	12.06.2006
Experimental team: Names	Addresses		
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Local Contact:	E. Kentzinger		

Experimental report text body

The purpose of this experiment was to measure two samples in the framework of the HGF SANS benchmarking. The two samples were:

- 1) A Polystyrene-block-Polyisoprene-block-Polystyrene (PS-PI-PS) Copolymer Thermoplastic
- 2) Silica spheres coated with stearyl alcohol in toluene

Those two samples were already measured on KWS-1 and KWS-2 by D. Schwahn. We report here on the results obtained on the PS-PI-PI sample.

The measurements were performed with entrance slit apertures of $2 \times 2 \text{ mm}^2$ (i.e., a wave vector transfer resolution δQ of $10^{-4} \text{ \AA}^{-1}$) and a beam size at sample position of 80×20 (width x height) mm^2 . The intensity at sample position was 300 n/s and the counting time 5 hours. After empty beam measurement, we deduced a transmission of 64 %. The radial average, subtracted from the empty beam, is depicted in Fig. 1.

We deduced a Q^{-4} dependency of the scattered intensity, in agreement with the KWS-1 and KWS-2 measurements performed at higher Q values (Top-right insert in Fig. 1).

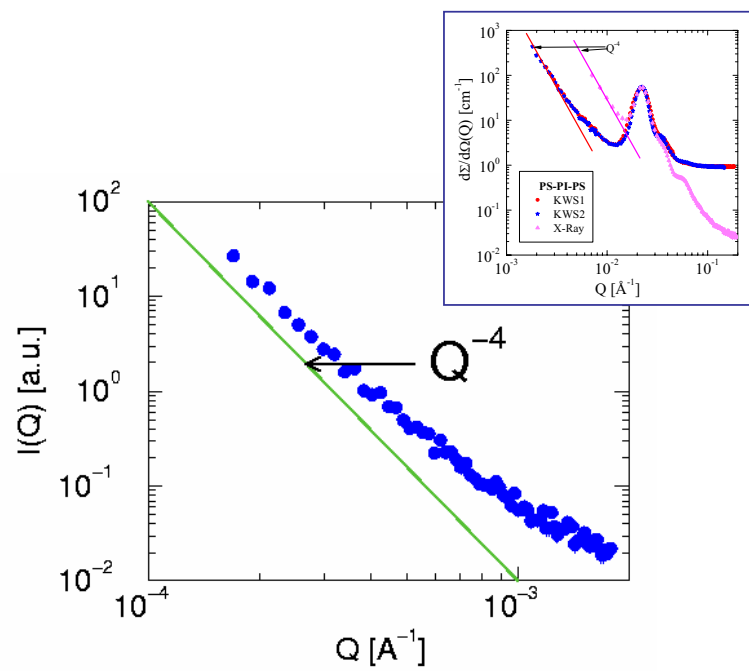


Fig. 1: Radial average of the very-small angle neutron scattering (V-SANS) measured at KWS-3 on a PS-PI-PS thermoplastic. Top-right: Radial averages obtained at KWS-1 and KWS-2