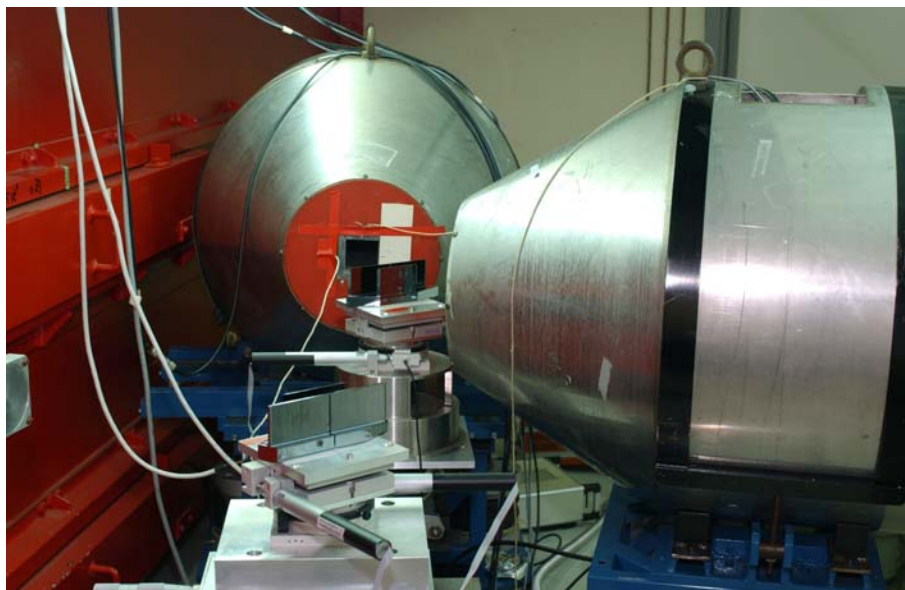


Double Crystal Diffractometer (DKD)



Instrument Parameters

<i>Beam tube:</i>	NLIIA straight guide cross section of guide 4.5 cm (height) $\times$ 3 cm (width)
<i>Monochromator:</i>	Si-crystal with coherent SiO ₂ precipitates or graphite
<i>Incoming beam</i> - <i>Cross section:</i> - <i>Sample size:</i>	$\approx 10 \text{ cm}^2$ 3 $\times$ 3 cm (max.)
<i>Neutron flux at sample:</i>	$> 10^4 \text{ n/s}$ (with graphite monochromator)
<i>Momentum transfer range:</i>	$2 \times 10^{-5} \text{ \AA}^{-1} \leq Q \leq 10^{-3} \text{ \AA}^{-1}$
<i>Ancillary equipment:</i>	heater device and pressure cell as for KWS1

Instrument Responsible

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

Proposal number:	DKD-04-005, KW3-04-016		
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:	09.09.04 – 24.09.04 11.03.05 – 15.03.05 19.04.05 – 22.04.05 19.05.05 – 23.05.05	Date of report:	29.05.06
Experimental team: Names	Addresses		
Aurel Radulescu, Emmanuel Kentzinger, Jörg Stellbrink, Dietmar Schwahn, Manfred Heiderich	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr. E.Kentzinger, Dr.D.Schwahn		

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.

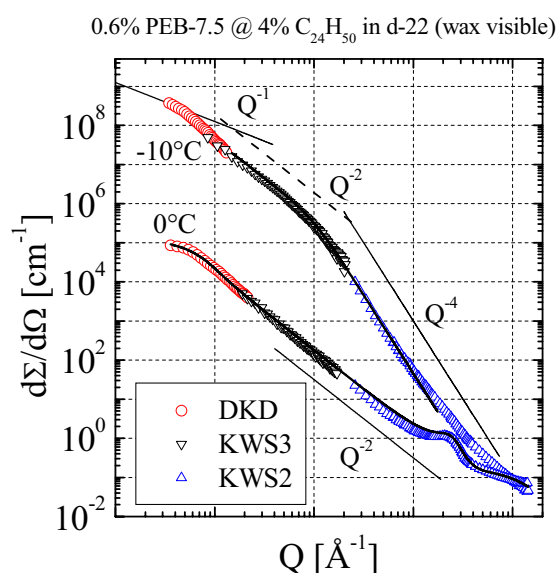


Fig.1 - Scattering patterns under wax contrast from a mixed solution of 0.6% low M_w PEB-7.5 copolymer and 4% C_{24} wax in decane.

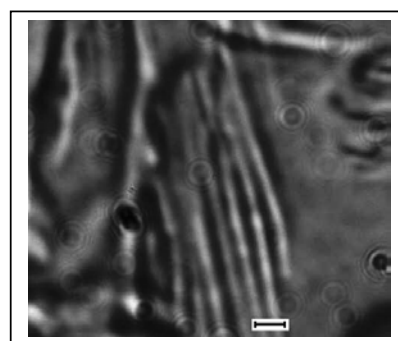


Fig.2 – A micrograph of the aggregates formed in the same solution at -10°C (scale bar $10 \mu\text{m}$).



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

Proposal number:	DKD-04-006		
Experiment title:	Determination of the main size of clay mesoscopic/macrosopic structures in archaeological and reference samples		
Dates of experiment:	20 days March/April 2005 09.11. – 10.11.2005	Date of report:	01-06-2006
Experimental team: Names	Addresses		
A. Botti	Univ. Roma TRE, Dip. Fisica "E. Amaldi", via della vasca navale 84, 00146 Roma (IT)		
Local Contact:	D. Schwahn, M. Heiderich		

Experimental report text body

A series of 18 reference pottery samples has been measured on DKD diffractometer: They differ from each other in terms of maximum firing temperature, heating rate and composition.

This experiment represents, in chronological order, last attempt at determining the main size of the grains which constitute the pottery bulk. Previous experiments on KWS2/PAXE and KWS3 failed because of the limitations in the minimum Q achievable, which made the determination of the grains R_g not reliable.

The data, collected in slit geometry, have been converted in pinhole geometry.

Multiple scattering effects have been minimized by drawing a tiny amount of pottery powder and depositing it on the surface of a scotch tape.

A selection of the data, which include a series of samples with fixed heating rate and composition but different temperatures, are shown in Figure 1 in a $\ln(I)$ vs Q^2 plot. By linear fitting the low Q range it is possible to estimate the main size of the structures which give rise to the scattering signal.

These values are represented in Figure 2 for different maximum firing temperature. Although slightly scattered a decreasing trend is clear.

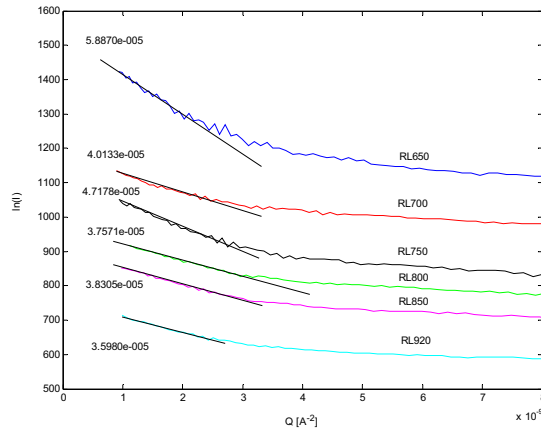


Figure 1: $\ln(I)$ vs Q^2 for samples with a reddish clay material, fired at slow heating rate at different maximum firing temperature. Lines are the best linear fits.

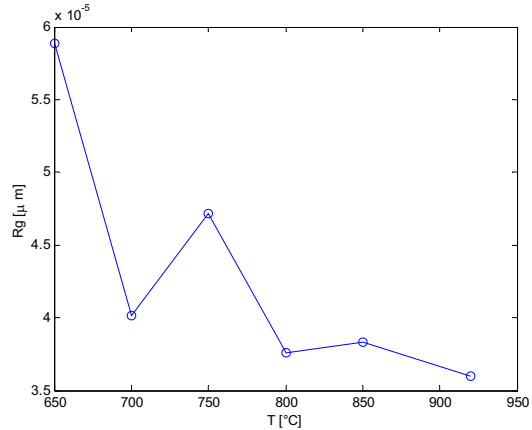


Figure 2: Dependence of the grain R_g on the maximum firing temperature. The samples are the same of Figure 1.

The results of previous experiments (not shown) on the SANS and USANS instruments were compatible with two scenarios: the grains have a rough surface which is quantified by a power law exponent (d) and a typical main size, R_g , (or distribution of sizes) and these two parameters are not correlated one with the other [1]; Or the firing process can be described by a growing process. According to the latter scenario firing process, and in particular the maximum firing temperature, changes the grain distribution: the small grains melt in the bigger ones. This process lowers the intensity at high Q and increases the intensity at low Q and thus giving an increasing d exponent; as it has been seen in SANS measurements [1]. Such process should, at the same time, shift the R_g parameter to higher values and push the bending point in the measured intensity to lower Q values. According to the present results of the DKD experiment the growing mechanism has to be rejected: the grains, as shown in Figure 2 diminish their average sizes while temperature increases. This is an evidence that excludes an effect of the change of the grains size distribution on the value of the power law exponent. The average size of the clay grains falls in the micrometer range.

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



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

Proposal number:	DKD-06-001, KW3-06-003		
Experiment title:	Large scale size morphology of alternating copolymers in solution (parts 1 and 2)		
Dates of experiment:	11.03.06-15.03.06	Date of report:	29.05.06
Experimental team: Names	Addresses		
Aurel Radulescu	Forschungszentrum Jülich Institut für Festkörperforschung D-52425 Jülich Germany		
Local Contact:	Dr.E.Kentzinger, Dr.D.Schwahn		

Experimental report text body

Recently, SANS studies have revealed that in dilute solution upon cooling the random copolymers PEB- n (where n represents the number of ethyl side branches per 100 backbone carbon) form 1-dimensional aggregates which, depending on the crystalline degree of the copolymer tuned by n , are either open objects (like for PEB-11) or present a longitudinal alternation of crystalline and amorphous sequences (like for PEB-7.5) [1,2]. A similar behaviour is shown by the PE-PEP crystalline amorphous star polymers with the crystallisable PE blocks in the star center [1] and by the alternating isotactic-atactic polypropylene (iPP-aPP) copolymers [3]. Thus, the general morphology of self-assembling materials with multiple alternating crystalline and amorphous blocks appears to be rodlike instead of 2-dimensional which is favoured by the crystalline-amorphous diblock architecture. Focusing SANS (f-SANS) and ultra SANS (u-SANS) investigations complimented by microscopy observations have shown that the PEB- n random copolymers form multilevel morphologies and, besides the 1D aggregates form additionally large structures with sizes within the micrometer length scale. Stimulated by these conclusions and also by the microscopy observations of some large scale soft aggregates formed by the alternating iPP-aPP copolymers in dodecane solution (Fig.1) we performed new f-SANS and u-SANS investigations of the self-assembling behaviour of these materials in solutions. Structural measurements involving the KWS-3 and DKD instruments have been performed on 1% polymer solution in dodecane at room temperature. The data collected at the DKD instrument in slit-geometry have been transformed into pin-hole geometry using the procedure described in [4]. Then, the scattering patterns from the iPP-aPP aggregates in solution have been analysed over the whole Q range covered by combining the conventional-, focusing- and ultra-SANS instruments at FRJ-2 reactor, namely $3 \times 10^{-5} \div 0.2 \text{ \AA}^{-1}$. These results are presented in Fig.2 and reveal a multilevel organization of the polymers: at a lower length-scale the polymers aggregate by yielding 1D objects whose characteristic scattering exhibits a Q^{-1} power law behaviour. The thickness and the density of these aggregates have been evaluated elsewhere [3]. At a larger length-scale (larger than $2\pi/Q^*$, where Q^* is

marked in the figure) a second kind of aggregates occurs and gives rise to the scattering revealed at low Q by f-SANS and u-SANS. These must be the spherulitic-like soft aggregates revealed by the micrographs. We may conclude that a hierarchy of structures appears in this case, the formation of large-scale aggregates being a result of the association of many 1D thin aggregates. The Q^{-4} behavior of the scattering from the soft large scale aggregates is not yet understood as long as such behavior is typical for the scattering of compact structures showing sharp interfaces with the environment. The analysis and interpretation of the experimental data is in progress.

References: [1] D.Schwahn et al., *Macromolecules* 35, 861, 2002; [2] A.Radulescu et al. *J.Pol.Sci. B Pol.Phys.* 42, 3113, 2004; [3] A.Radulescu et al. *Macromolecules* 37, 6962, 2004; [4] D.Schwahn, and M.H.Yoo, *Springer Proceedings in Physics* vol.10, Springer Verlag: Berlin, Heidelberg, New York, Tokyo, 1986, p 83

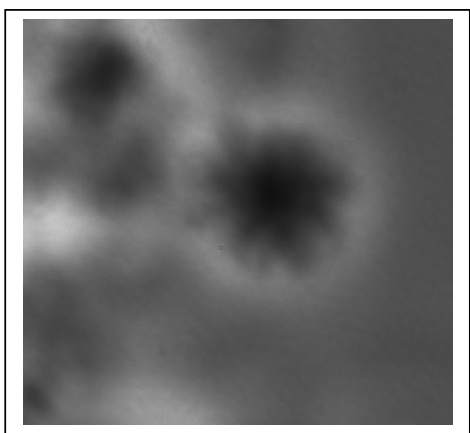


Fig.1 – Micrograph of the aggregates formed by the iPP-aPP alternating copolymers in dodecane at room temperature; the size of the spherulitic-like soft aggregate is about 4 μm .

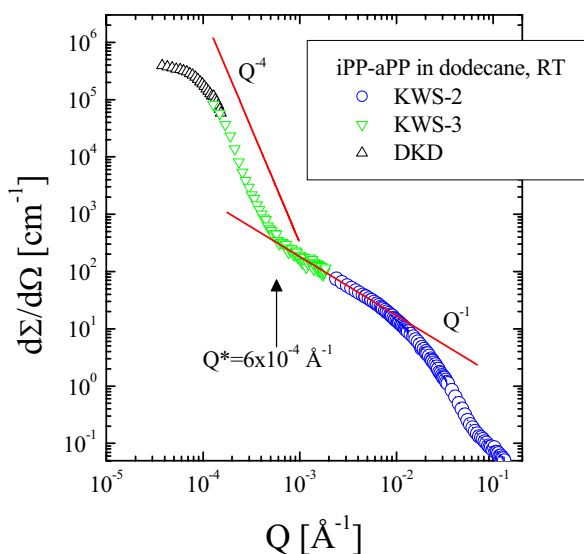


Fig.2 – Wide- Q scattering pattern from aggregates of iPP-aPP copolymers in dodecane collected at room temperature by combining conventional-, focusing- and ultra-SANS.