

High Resolution Backscattering Spectrometer (BSS)



Instrument Parameters

Beam tube:	NLI, cold neutrons, straight guide, 10 cm (height) $\times$ 7 cm (width)
Beam size at sample:	3.5 cm $\times$ 3.5 cm
Neutron flux at sample:	10^4 n/cm ² s
Background:	$\approx$ 8 counts/h
Monochromators:	Si(111), Si _{0.9} Ge _{0.1} (111)
Analyser:	Si(111)
Detectors:	nine ³ He counters, one ³ He monitor
Incident energy:	2.08 meV Si(111), 2.07 meV Si _{0.9} Ge _{0.1} (111)
Incident wavelength:	6.271 Å Si(111), 6.30 Å Si _{0.9} Ge _{0.1} (111)
Energy transfer range:	−15 ... 15 μ eV Si(111), −29 ... 1 μ eV Si _{0.9} Ge _{0.1} (111)
Energy resolution (FWHM):	1.2 ... 2.4 μ eV Si(111), $\approx$ 2 μ eV Si _{0.9} Ge _{0.1} (111)
Elastic Q-range:	0.2 ... 1.9 Å ^{−1}
Q-resolution:	0.05 Å ^{−1} ... 0.25 Å ^{−1}
Sample environment	orange cryostat 2 ... 300 K; closed cycle cryostat 12 ... 350 K; cryofurnace 80 ... 750 K; furnace 300 ... 1900 K

Instrument Responsible:

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

Proposal number:	BSS-04-016, BSS-05-020		
Experiment title:	Rotational dynamics of methyl groups in the chloranilic acid plus tetramethylpyrazine complex: the influence of deuteration of the H-bond		
Dates of experiment:	02.09.2005, 1 day	Date of report:	25.02.2006
Experimental team:			
Names	Addresses		
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Local Contact:	H. Grimm		

Experimental report text body

The charge transfer/hydrogen bond system chloranilic acid (CLA) plus tetramethylpyrazine (TMP) was successfully studied in a previous experiment [1]. The present work intends to investigate the effect of deuteration of the hydrogen bond linking the two molecular constituents. Due to the central role of such hydrogen bonds for the properties of charge transfer materials we expect characteristic changes from the interplay of lattice contraction, molecular reorientation and charge redistribution.

While the fully protonated material was investigated with the SiGe offset monochromator of the instrument in the energy range $-33 < \Delta E [\mu\text{eV}] < +3$ at an energy resolution $\delta E = 1.9 \mu\text{eV}$ [1] the deuterated compound is investigated at exactly the same configuration of the instrument (fig. 2) and with improved energy resolution $\delta E = 1.1 \mu\text{eV}$ in a symmetric energy range $-18 < \Delta E [\mu\text{eV}] < +18$ using the Si[111] monochromator. Such spectra contain only the inner tunnelling lines Fig. 1). Fig. 2 shows that the band at $29 \mu\text{eV}$ is almost unaffected from deuteration while the band at $19 \mu\text{eV}$ is clearly shifted to lower energies, cf. ref. 2. The shift of the $29 \mu\text{eV}$ band follows an Arrhenius dependency with activation energy of about 8.6 meV which is very similar to that of the protonated material. The Fig. 1 shows a comparison of the inner tunnelling lines of the protonated (xxx) and deuterated (ooo) material. Instead of one strong tunneling band at $3.3 \mu\text{eV}$ in TMP:h-CLA we observe a doublet with one transition at slightly higher, the other at clearly lower energy. A very rough estimate on the corresponding potential barriers based on a pure $\cos(3\phi)$ potential leads to changes of -1.5% and $+6.8\%$, respectively.

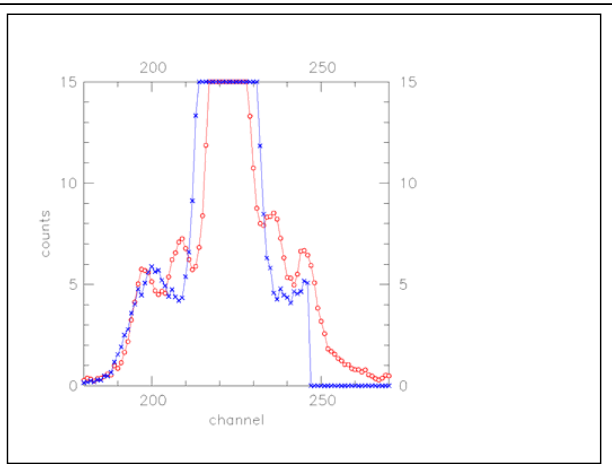


Fig. 1 Tunnel spectra of TMP:h-CLA (xxx) and TMP:d-CLA. for TMP:h-CLA the accessible energy range ends at $-3\mu\text{eV}$.

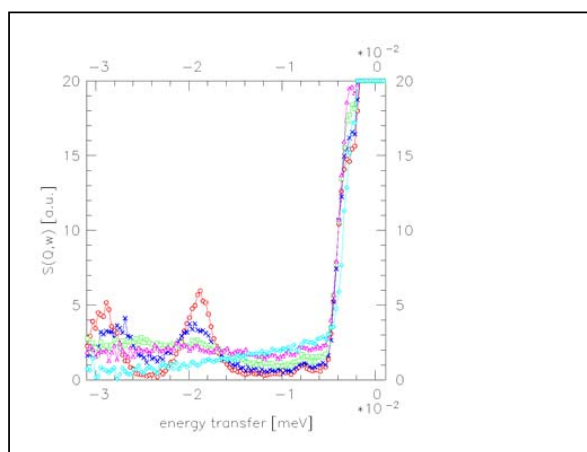


Fig. 2 Temperature dependence of the high energy tunnelling Bands in TMP:CLA-d2. T=4.5K (red) to 31K(cyan).

The comparison with the pure donor compound TMP has shown [1] that the methyl rotational potential is significantly weaker in the TMP-CLA complex. This means that intermolecular interaction strongly contributes to the rotational potential. The dominance of steric effects is supported by an opposite change of the hindering barrier observed in 2,6-DMP-CLA [2]. Deuteration of the hydrogen bond on the other hand is not expected to change the geometry of the environment significantly. Therefore the observed change is not unlikely to be due to effects of charge redistribution.

A comprehensive analysis of all spectra is under way. As in earlier cases it shall be based on a full quantum mechanical treatment of the lattice dynamics in three dimensions [3].

[1] M Prager, A Pawlukoje, L Sobczyk, E Grech, H Grimm, J. Phys.: Condens. Matter 17,5725(2005)

[2] Experimental report FRJ2 2005, BSS-05-028

[3] M.R. Johnson, M. Prager, H. Grimm, M.A. Neumann, J. Kearley, C.C. Wilson, Chem. Phys. 244,49(1999)

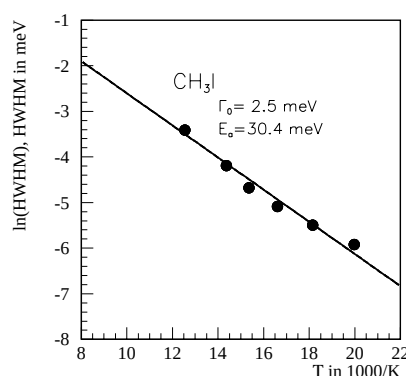
Experimental Report
of Neutron Scattering Experiments
at the FRJ-2 Reactor

Proposal number:	BSS-04-017		
Experiment title:	Quasi-elastic neutron scattering of methyl iodide		
Dates of experiment:	09. - 15.05.2005	Date of report:	03.03.2006
Experimental team:			
Names:	Addresses:		
Oliver Kirstein Michael Prager Hans Grimm	Bragg Institute, ANSTO, Menai, NSW 2234, Australia Institut für Festkörperforschung, FZJ, D-52428 Jülich, Germany Institut für Festkörperforschung, FZJ, D-52428 Jülich, Germany		
Local contact:	Hans Grimm		

Usually, the dynamics of the majority of rotating groups in molecular crystals can be described by a mean-field model known as the Single Particle Model (SPM) [1]. An analysis of experimental results which goes beyond a phenomenological use of the SPM must be able to explain the rotational potential, which determines the dynamics of the rotating group, based on the crystal structure and the fundamental interatomic and intermolecular interactions. There are different ways of modeling the dynamics of molecules by using e.g. ab-initio, DFT, force-field and quantum chemistry or transferable pair-potential calculations. The latter method was used to describe the lattice and rotational dynamics of the methyl halides by using pair potentials based on Universal Force Fields (UFF) [2]. Values that characterize the potential, which determines the dynamics of the rotating group such as the tunneling frequency and transition to the first librational state were calculated and compared to the earlier experimental results already mentioned [3]. In order to complete the experiments done so far quasi-elastic neutron scattering experiment on methyl iodide was performed in order to obtain values for the activation energies. The results will be used for comparison with calculations and to refine or determine potential parameters. The sample is available from commercial suppliers such as Aldrich with a chemical purity $\geq 99.55\%$ and was used in the experiments without any further purification. The scattering probability of the sample was approximately 25%. The experimental data obtained using the backscattering spectrometer BSJ in its standard configuration (i.e. Si(111) monochromator, incident energy 2.08 meV, energy transfer $\pm 17 \mu\text{eV}$) were transformed into $S(Q, \omega)$ using standard programs in order to derive the relevant physical parameters in this case the width of the quasi-elastic Lorentzian contribution to the spectrum.

The evaluation involved the following steps

- Subtraction of the background
- Determination of the resolution function
- Convolution of the theoretical spectrum with the resolution function
- Fit of the convoluted spectra to the measured data



The temperature dependent linewidth of the Lorentzian is shown in the figure above in which the logarithm of the HWHM is plotted versus $1000/T$ (HWHM in meV, T in K). By applying a least squares fit to the data we obtain an attempt frequency of $\Gamma_0 = 2.5(\pm 0.8)$ meV. This value is in agreement with attempt frequencies of other compounds containing CH_3 groups. The activation energy, which is the difference between the height of the rotational potential and the ground state is $E_a = 30.4(\pm 2.3)$ meV. Taking the previously measured tunneling and the librational transitions of $2.44 \mu\text{eV}$ and 14.57 meV, respectively, we obtain for the three- and sixfold terms of the Fourier-expansion of the rotational potential the following combination $(V_3, V_6) = (41.4 \text{ meV}, 1.6 \text{ meV})$. This combination allows to calculate an activation energy of $E_a = 33.5$ meV. There is good agreement between the theoretical SPM model and the experiment indicating that the dynamics can be well described by applying the SPM approach.

References

- [1] W. Press, Single Particle Rotations in Molecular Crystals, Springer Tracts in Modern Physics (Springer, Berlin 1981), Vol. 81
- [2] A. K. Rapp, C. J. Casewitt, K. S. Colwell, W. A. Goddard III, W. M. Skiff, J. Am. Chem. Soc., Vol 114, No. 25, 1992
- [3] O. Kirstein, M. Prager, J. Chem. Phys., Vol. 120, No. 11, 5199 (2004)



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

Proposal number:	BSS-04-019		
Experiment title:	Dynamic Miscibility Effects in a Blend of Polymers with Very Different T _g		
Dates of experiment:	17/01/2005-01/02/2005	Date of report: 08/02/2005	
Experimental team: Names	Addresses		
Caroline Genix Juan Colmenero Arantxa Arbe Dieter Richter	Donostia International Physics Center, Apdo. 1072, 20080 San Sebastian, SPAIN Dpto. de Física de Materiales, UPV/EHU, , “ , “ , “ Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ IFF, FZJ, Jülich, Germany		
Local Contact:	Andreas Wischnewski		

Experimental report text body

The aim of this experiment was to investigate the effect of blending on the dynamical behaviour of a polymer. The system chosen was poly(ethylene oxide) / poly(methyl methacrylate) (PEO/PMMA), which has the advantage to show very different glass transition temperatures T_g for each of the pure components (PEO: T_g=213K; PMMA: T_g=400K). By backscattering we wanted to follow the scattering dominated by the incoherent contribution of the hydrogens of the protonated component in the blend, where the other component is deuterated, and compare these results with those obtained for the pure homopolymers.

The BSS measurements have been performed on the following samples: pure PEO (fully protonated) at 4, 300, 350, 375 and 400K, and two blends of PEO/PMMA (25%/75%), where one of the two components was protonated (h) and the other deuterated (d). For hPEO-dPMMA we investigated 4, 300, 325, 350, 375, 400, 425, 450 and 500K, and for dPEO-hPMMA 4, 350, 400 and 450K. This corresponds to the region well above the glass transition for PEO but close or below to that of PMMA.

The samples were placed in Aluminum flat containers at 45° with respect to the incident beam. The thicknesses were such that a transmission of ≈ 0.9 was calculated. With $\lambda=6.27\text{\AA}$ a Q-range of $0.16 \dots 1.87\text{\AA}^{-1}$ was accessed and an energy window of $\pm 17\mu\text{eV}$ was explored. Reasonable statistics was achieved with measuring times of about 18 hours. Vanadium and empty cell measurements were also carried out to correct the spectra.

For $Q=0.56\text{\AA}^{-1}$ Fig. 1 shows the spectra corresponding to PEO pure and in the blend at 350 and 400K. A clear slowing down in the dynamics of PEO is observed as effect of blending. A quantitative analysis of the spectra in terms of stretched exponential functions is currently being performed.

On the other hand, the dynamical behaviour of the PMMA component at temperatures close to the glass transition of the pure PMMA seems to be dominated by the rotation of its α -methyl group. This is shown in Fig. 2, where we have described the scattering curves by assuming that the main chain and ester methyl groups contributions are just elastic (that for the ester methyl group is modulated by the EISF, since its rotation is very fast at these temperatures [1]).

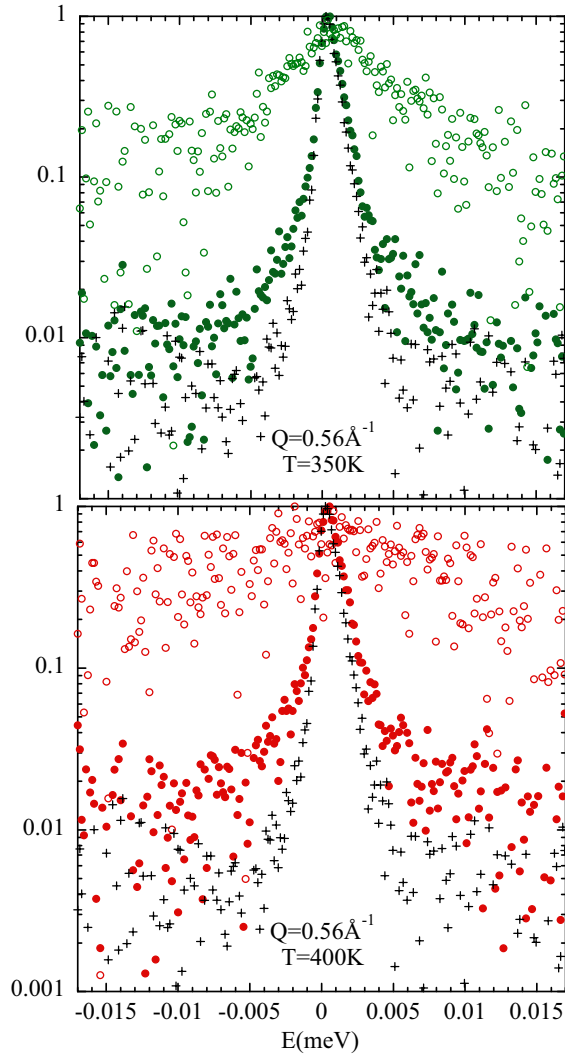


Fig. 1: Scattering function measured at $0.56 \text{ \AA}^{-1}$ for pure PEO (protonated) (empty symbols) and the blend containing 25% of protonated PEO in a deuterated PMMA matrix (full symbols): 350K (upper) and 400K (lower). The functions are normalized to their maximum intensities. The resolution function is displayed by the crosses.

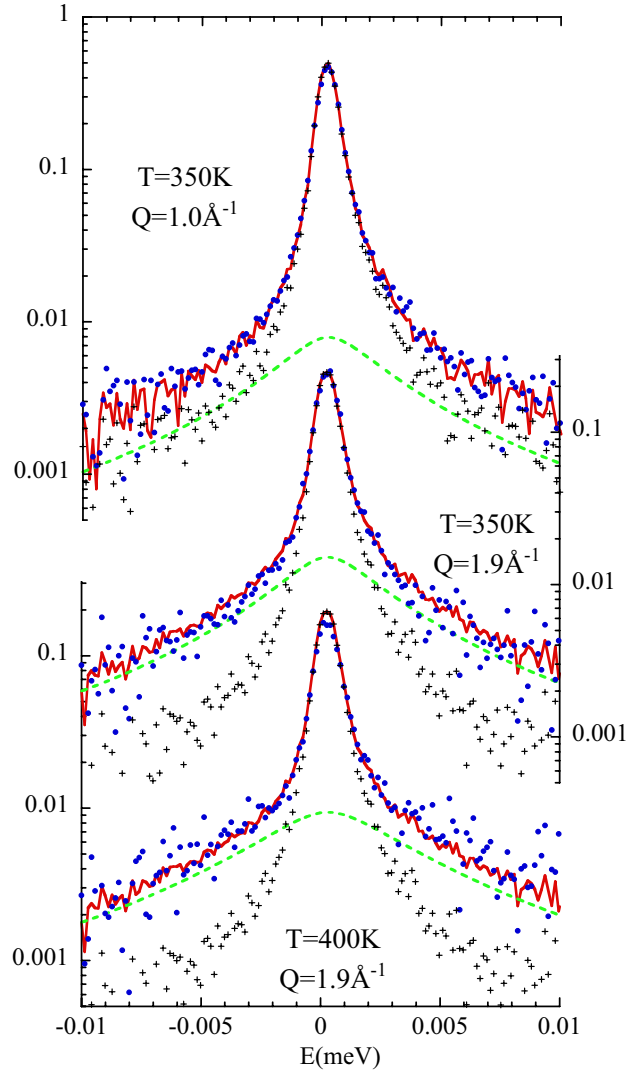


Fig. 2: Spectra obtained from a sample containing 75% of protonated PMMA and 25% of deuterated PEO at the Q-values and temperatures indicated. Solid lines: descriptions assuming the rotation of the α -methyl groups in PMMA as the only origin of the quasielastic broadening. Dotted lines: quasielastic contributions. Crosses: resolution.

References:

- [1] A. J. Moreno, A. Alegría, J. Colmenero, B. Frick, *Macromolecules* **34**, 4886 (2001)



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

Proposal number:	BSS-04-023		
Experiment title:	Superparamagnetism in hematite nanoparticles		
Dates of experiment:	14.-23. 4. 2005	Date of report:	29. 05. 2005
Experimental team: Names	Addresses		
Christian R. H. Bahl Kim Lefmann	Materials Research Department, AFM-228 Risø National Laboratory Frederiksborgvej 399 DK-4000 Roskilde Denmark		
Local Contact:	Andreas Wischnewski		

Experimental report text body

The finite size of magnetic nanoparticles ensures that they are single domain particles, and will introduce spin dynamics, which are absent in bulk materials. The magnetisation direction may reverse spontaneously when the thermal energy is near the energy barrier given by the easy-axis anisotropy, so-called superparamagnetism (SPM). It is also possible to induce collective magnetic excitations, where the spins oscillate coherently around the easy-axis in quantised energy levels. The spacing between these gives rise to inelastic resonance peaks. Usually, the superparamagnetic relaxation is much slower than the collective magnetic excitation precessions. However, at elevated temperature when the two time scales become comparable a new relaxation regime is predicted to occur: isotropic relaxation of the spins. This should be observed as a dramatic reduction in the neutron scattering signal from the magnetic Bragg reflections. However, despite this extreme dynamic spin relaxation coherent magnetic order is still maintained in the nanoparticle, due to the strong exchange coupling within it.

We have studied two samples of 8 nm canted antiferromagnetic hematite (α -Fe₂O₃). One that was prepared by drying an aqueous suspension of particles, and one prepared by coating the nanoparticles with a layer of phosphate before drying, to minimize the (exchange) interactions between the individual particles.

The characteristic time between the spontaneous flipping of the spins is given by an Arrhenius-type equation. This flipping time results in a broadening of the quasi-elastic peak at the antiferromagnetic scattering vectors with a Lorentzian line shape. This broadening we have previously measured by neutron scattering at Rita2 (Paul Scherrer Institute, Switzerland). But due to poor resolution and overlap from the collective magnetic excitation signals at ± 0.2 meV, the width of the peak has been difficult to measure.

The high resolution of the BSS and positions of the collective magnetic excitation signals far beyond the limits of the BSS energy scale, have now enabled us to measure the width of the quasi-elastic peak more confidently.

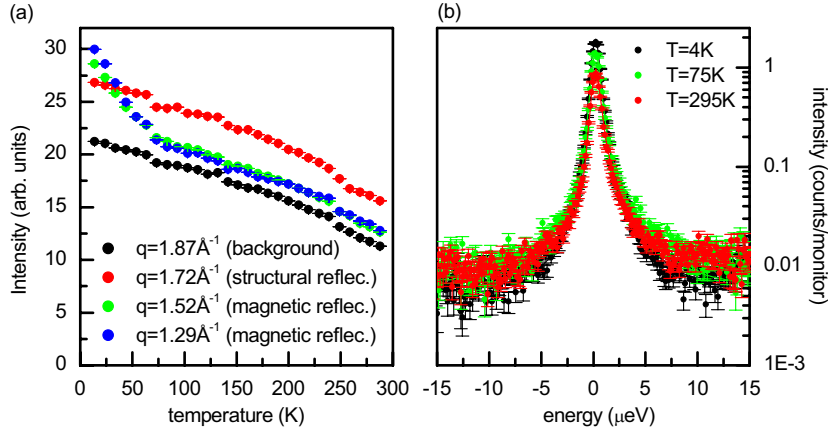


Figure 1. Measurements acquired for the sample of weakly interacting hematite nanoparticles: (a) Elastic temperature scans at two antiferromagnetic reflections at $q=1.29\text{\AA}^{-1}$ ($1.37\text{\AA}^{-1}$) and $1.52\text{\AA}^{-1}$ ($1.51\text{\AA}^{-1}$) and a structural at $1.72\text{\AA}^{-1}$ (the q -values in () indicate the positions of the Bragg reflections). Clearly, the BSS setup is ideal for measuring hematite. (b) Inelastic energy scans at $q=1.29\text{\AA}^{-1}$, $T=4, 75, 295\text{K}$. Fits to the data are represented by the full lines.

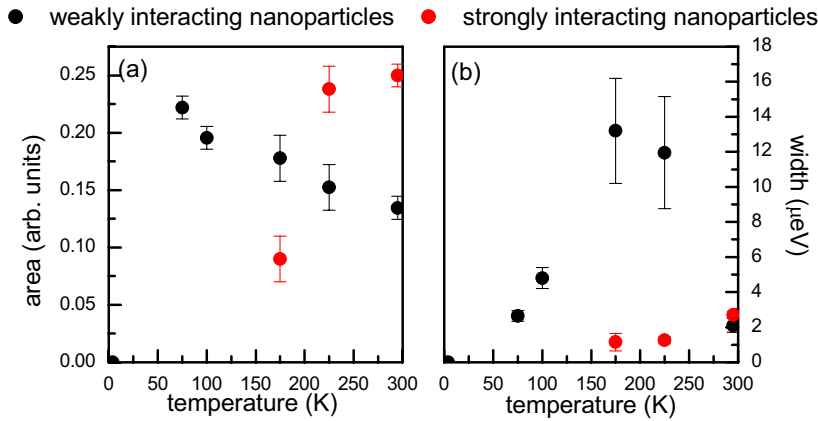


Figure 2. Integrated area and width of the quasi-elastic signal as a function of temperature as determined from the fits.

The preliminary analysis of the inelastic neutron scattering data shows the expected decrease of the integrated area of the quasi-elastic signal with temperature (Fig. 2(a)). However, the important detail documenting the change into the isotropic relaxation regime is shown by the width of the quasi-elastic peak as a function of temperature (Fig. 2(b)). The width increases up to $T \sim 175\text{K}$ as expected for superparamagnetic relaxation (thermally induced), but then it dramatically decreases for $T > 175\text{K}$. We have performed a few measurements on the sample of strongly interacting hematite nanoparticles (the interactions are known to block the magnetic relaxations), these indeed show that the SPM-isotropic relaxation crossover sets in at a higher temperature than for the weakly interacting nanoparticles.

Further data analysis and more experimental investigations are needed to determine the details of the SPM-isotropic relaxation mechanisms, the effect of inter-particle interactions and nanoparticle size, and thereby allowing us to experimentally prove the existence of isotropic spin relaxation in magnetic nanoparticles.



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

Proposal number:	BSS-04-025		
Experiment title:	Dynamic miscibility in miscible polymer blends		
Dates of experiment:	27 – 31 January 2005	Date of report:	5 December 2005
Experimental team: Names	Addresses		
Juan Colmenero Arantxa Arbe Roberto Pérez Aparicio Dieter Richter	Dpto. de Física de Materiales, UPV/EHU, Apdo. 1072, 20080 San Sebastian, SPAIN Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ Dpto. de Física de Materiales, UPV/EHU, Apdo. 1072, 20080 San Sebastian, SPAIN IFF, FZJ, Jülich, Germany		
Local Contact:	HANS GRIMM		

Experimental report text body

Motivated by the question of the dynamic miscibility in polymer blends (see, e.g., [1-3]), the main goal of our general project was to investigate the effect of blending on the dynamical processes in the polymer blend head-to-head polypropylene / poly(ethylene propylene) (HHPP/PEP) ($T_g(\text{HHPP})=248\text{K}$, $T_g(\text{PEP})=213\text{K}$). Taking advantage of isotopic labeling, the dynamics of both components in the blend could be isolated by means of quasielastic neutron scattering. A first set of measurements were performed at the backscattering spectrometer IN16 (ILL, Grenoble). There, both homopolymers and a 50%/50% blend where the PEP component was fully deuterated (h-HHPP/d-PEP) were investigated. In this way we characterized the dynamical processes for the two pure systems and the effect of blending on HHPP (the high- T_g component). We established that, while the methyl group rotations observed in the glassy state are not affected by blending, the subdiffusive atomic motions in the segmental relaxation regime become faster in the presence of PEP chains. Unfortunately, synthesis problems with deuterated HHPP prevented the experimental isolation of the PEP component in the blend. Nevertheless, with the information on the dynamical behavior of HHPP in the blend provided by the IN16 experiments at hand, we could in principle deduce the dynamics of PEP in the blend from measurements on the fully protonated sample. This was the aim of this experiment.

We thus investigated the 50%/50% HHPP/PEP blend, where both components were fully protonated, by means of BSS with $\lambda=6.271\text{\AA}$ in the Q-range $0.16 \leq Q \leq 1.87 \text{\AA}^{-1}$. Measuring times were of about 19 hours per T. The thickness of the sample was such that a transmission of 0.9 was calculated (0.2 mm). The temperatures investigated were 300, 325, 350, 375 and 400 K (all of them above the glass transition of the blend, $T_g \approx 228\text{K}$). The instrumental resolution of the spectrometer was determined from the sample at 4K. Measurements of background and Vanadium were performed in order to correct the data.

The spectra obtained for the fully protonated blend (see an example in Fig. 1) reflect the dynamics of hydrogen atoms from both blend components. A first global description of the spectra delivered timescales in between those determined for HHPP in the blend and pure PEP (see Fig. 2), indicating a very fast dynamics for PEP in the blend. A further analysis of the data considering the information of HHPP dynamics in the blend leads to the timescales shown in Fig. 2 as empty squares for the PEP component in the blend. It seems that PEP dynamics is hardly affected by blending. Figure 1 shows the both components of the blend after the analysis performed.

The extremely weak influence of blending on the low- T_g component dynamics of this system was not expected (see, e.g., [1]). Therefore, further analyses and/or new measurements are necessary in order to establish well these results.

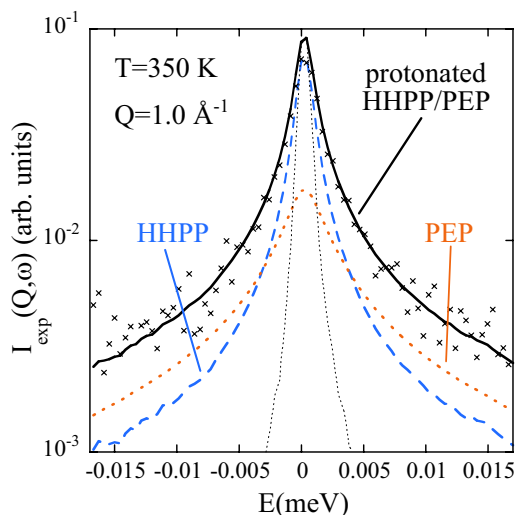
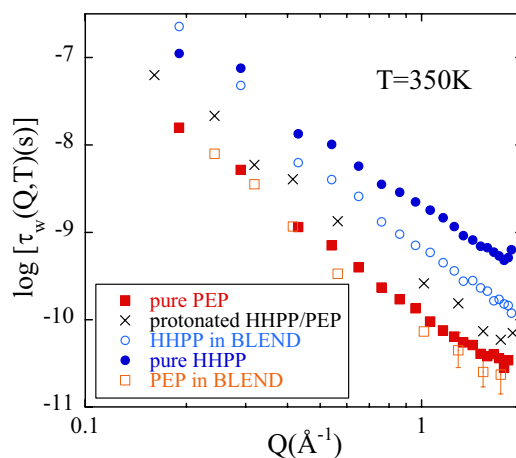


Fig. 1: Scattering function in logarithmic scale for the fully protonated HHPP/PEP blend at $Q = 1.0 \text{ \AA}^{-1}$ and 350K. The solid line is a fitting curve. Dashed line depicts the HHPP contribution imposed from previous IN16 results and dashed-dotted the PEP contribution deduced. The dotted line shows the instrumental resolution.

Fig. 2: Momentum-transfer dependence of the characteristic times for segmental dynamics obtained at 350 K for HHPP hydrogens in the homopolymer (full circles, IN16) and in the blend h-HHPP/d-PEP (empty circles, IN16), and for PEP hydrogens in the homopolymer (full squares, IN16) and in the blend with HHPP (empty squares, BSS). The crosses show the global timescale obtained when the BSS HHPP/PEP (fully protonated) spectra are described by a single stretched exponential.



REFERENCES

- [1] T. P. Lodge and T. C. B. McLeish, *Macromolecules* **32**, 5278 (2000).
- [2] I. Cendoya, A. Alegría, J. M. Alberdi, J. Colmenero, H. Grimm, D. Richter, B. Frick, *Macromolecules* **32**, 4065 (1999).
- [3] S. Hoffmann, L. Willner, D. Richter, A. Arbe, J. Colmenero, B. Farago, *PRL* **85**, 772 (2000).
- [4] W. W. Graessely et al., *Macromolecules* **28**, 1260 (1995).
- [5] The partial structure factors of hhPP and PEP have already been investigated by us at FRJ-2 Reactor in Exp. Rep. DNS-04-008 (2004).



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

Proposal number:	BSS-04-027		
Experiment title:	Neutron backscattering on nanoconfined poly(methyl phenyl siloxane)		
Dates of experiment:	16.02.–15.03.2005	Date of report: 24.03.2006	
Experimental team: Names	Addresses		
Dr. Schönhals, A. Dr. Zorn, R. Mayorova, M.	Bundesanstalt für Materialforschung und –prüfung, Unter den Eichen 87, 12205 Berlin Forschungszentrum Jülich, Institut für Festkörperphysik Forschungszentrum Jülich, Institut für Festkörperphysik		
Local Contact:	M. Zamponi, A. Wischnewski		

Experimental report text body

The influence of a spatial nano-confinement on both the methyl group rotation and the microscopic dynamics of the glass-forming polymer poly(methyl phenyl siloxane) (PMPS) (glass transition temperature $T_g = 213$ K) was investigated. Dielectric spectroscopy shows that the segmental dynamics of PMPS is accelerated close to T_g compared to the bulk (confinement effect). Moreover a transition from a Vogel-Fulcher-Tammann-like temperature dependence of the relaxation time to an Arrhenius type is found for a pore size of 5 nm indicating a change in the dynamics. This also supported by DSC experiments. Incoherent inelastic neutron scattering (NS) was carried out on PMPS confined to Sol/Gel-glasses (pore sizes: 7.5, 5.0, 2.5 nm) and on a bulk sample as reference.

The glasses were treated in vacuum to remove impurities. The polymer was injected into the vacuum chamber and the pores were filled by capillary wetting. The experiments were done on the back scattering spectrometer (BSS) (wave length of $\lambda = 6.271$ Å, energy resolution of 1 μ eV; energy transfer range of 17 μ eV). To have a broader time range additional experiments were carried out on the Time-of-Flight spectrometer IN6 and on the backscattering instrument IN16 at the Institut Laue Langevin (ILL, Grenoble France). The spectra were corrected with data obtained for an unfilled nanoporous glass (5 nm) sealed under a He atmosphere.

Fig. 1 depicts the incoherent intermediate scattering function $S_{inc}(Q,t)$ for confined PDMS at $T = 120$ K. The points between 0.5 ps and 20 ps originate from the Fourier transform of IN6 data; those at $t > 150$ from BSS/Jülich. The data are analysed by fitting the KWW-function to the data where $A(Q)$ is the Elastic Incoherent Structure Factor (EISF) for the methyl group dynamics and DWF is the Debye-Waller

factor: $S_{Inc}(Q, t) = DWF \cdot ((1 - A(Q)) \exp(-t/\tau)^\beta + A(Q))$. For decreasing pore size the EISF increases due to an increasing amount of immobilized CH_3 groups probably located in a boundary layer at the pore walls. Fig. 2 compares the relative amount of the immobilized CH_3 groups in confinement versus inverse pore size for PMPS and poly(dimethyl siloxane) (PDMS). For both polymers approximately the same pore size dependence is obtained. Therefore it is concluded that both polymers forming a boundary layer of similar thickness inside the pores.

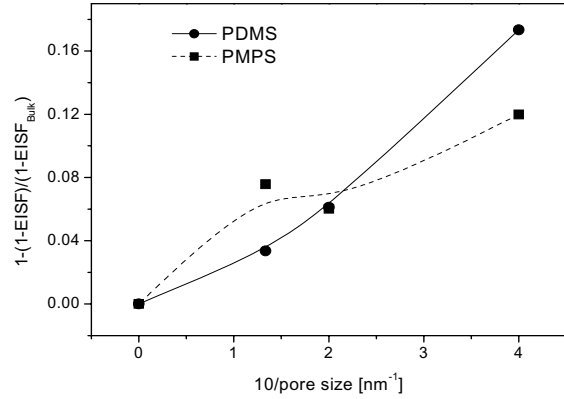
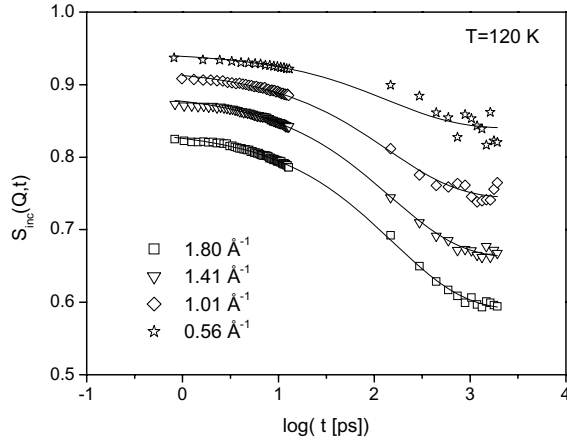


Fig. 1: $S_{Inc}(Q, t)$ for PMPS confined to pores of 7.5 nm. Lines are described in the text.

Fig. 2: Relative amount of the immobilized CH_3 groups versus inverse pore size.

Above T_g the decrease in $S_{Inc}(Q, t)$ is due to different processes which include vibrational contributions, methyl group reorientations and the segmental dynamics.

The ansatz $S_{Inc}(Q, t) = DWF \cdot ((1 - A) \exp(-(t/\tau_{CH_3})^{\beta_{CH_3}}) + A \exp(-(t/\tau_{Seg})^{\beta_{Seg}}))$ is used to analyze the data. The shape parameters β_{CH_3} and β_{Seg} are taken from an analysis of the CH_3 group rotation and from dielectric spectroscopy, respectively. Mean relaxation times are calculated by $\tau = \tau_{KWW} \Gamma(1/\beta)/\beta$. The relaxation times obtained by NS agree in both their absolute values and in their temperature dependence with those measured by dielectric and thermal spectroscopy. For the bulk and PMPS confined to 7.5 nm pores the temperature dependence of the relaxation times obeys the VFT-equation but the relation $\tau_{Seg}(T)$ for PMPS imbedded in pores crosses that of the bulk. This points to the fact that the thermodynamic state of the confined polymer is different from that of the bulk. For smaller pores sizes than 7.5 nm the temperature dependence of the relaxation time changes from a VFT to an Arrhenius-like behaviour. It is concluded that the character of the underlying fluctuations is dramatically changed and that an intrinsic length scale is relevant for glassy dynamics to appear in PMPS.



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

Proposal number:	BSS-05-001		
Experiment title:	Methyl rotational dynamics in acetone-D ₂ O clathrate		
Dates of experiment:	2.4.2005, 7 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
M. Prager	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	H. Grimm		

Experimental report text body

Due to the weakness of interaction with its environment acetone in acetone-water clathrate is expected to represent a guest molecule with a methyl rotational potential and methyl-methyl coupling predominantly caused by intramolecular interaction [1,2,3]. Therefore the system can be modelled as a single particle problem and is in this form accessible to a simple mathematical treatment.

The actual experiment is a continuation of the experiment BSS-04-014. The formation of the clathrate structure after a dedicated annealing procedure could be proven by a modified vibrational density of states which was measured at the TOF spectrometer SV29. Such controlled samples were transferred to the BSS instrument and introduced cold into its cryostat. The samples do not show inelastic intensity in the energy regime $18 < \Delta E [\mu\text{eV}] < 18$ of the instrument. Additional annealing procedures led to no changes. This must mean that the internal barrier in the isolated acetone molecule is such strong that no tunnel splitting is observable. Gaussian98 calculations shall confirm this conclusion.

- [1] C. Gutt, W. Press, A. Hüller, J. Tse, H. Casalta, J. Chem. Phys. **114**,4160(2001)
- [2] M. Prager, J. Pieper, A. Buchsteiner, A. Desmedt, J. Phys. Condens. Matter **16**,7045(2004)
- [3] M. Prager, J. Baumert, W. Press, M. Plazanet, J.S. Tse, D.D. Klug, PCCP **7**,1228(2005)



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

Proposal number:	BSS-05-005		
Experiment title:	In vivo characterisation of selectively hydrogenated nucleic acids in deuterated Escherichia coli cells		
Dates of experiment:	19.06. – 25.06.2005	Date of report:	07/06/2006
Experimental team: Names	Addresses		
Joseph Zaccai Jasnin, Marion Tehei, Moeava	Institut Laue Langevin, Grenoble Cedex 9, France Institut de Biologie Structurale, Laboratoire de Biophysique Moléculaire, Grenoble, France CNR-INFM, Institut Laue Langevin, Grenoble Cedex 9, France		
Local Contact:	Zamponi, M.		

Abstract

A very slow cell water of *Haloarcula marismortui*, an extremely halophilic organism, was discovered on the backscattering spectrometer IN16 at ILL (Grenoble – France). In distinction to *E. coli* organism, K^+ was retained within the cells of *Haloarcula marismortui* even in the absence of metabolism. Therefore, it was hypothesized that the slow mobility of cell water in *Haloarcula marismortui* indicates a water structure responsible for the large and specific amounts of K^+ bound within these cells. In order to reinforce this hypothesis, we did the experiments on *E. coli* using the spectrometer BSS (FRJ-2, Jülich), which have about the same resolution then IN16. Data from BSS experiments on *E. coli* cells revealed that this extremely slow cell water do not exist in this organism.

Background

Water dynamics has been studied extensively by neutron scattering from the early days of the method [1]. In recent years the study has been extended to the water associated with proteins by using fully deuterated phycocyanin [2]. Diffusion in general and the dynamics of water inside cells are of considerable interest because crowding creates a local environment that is very far from the dilute conditions usually studied in biochemical and biophysical experiments. Many important questions have to be addressed. For example, is the crowding and association of water with intra-cellular structures different in different cell types? To what extent will additional 4M salt have an additional impact in the cytoplasm as it occurs in extremely halophilic archaeal cells? *Haloarcula marismortui* (*Hm*), an Archaeal species isolated from the Dead Sea, attracted our attention some years ago because of its high selectivity for K^+ (selectivity coefficient $K^+_{in} \cdot Na^+_{in} / K^+_{out} \cdot Na^+_{out}$, $\sim 20,000$) and because of the high permeability of the outer membrane. In distinction to the non-halophile cells *E. coli*, K^+ was retained within the cell even in the absence of metabolism. As the Na^+ has a half-time of exchange with the outside medium of less than 1 min while the K^+ has a time of exchange of over 24 h [3], it followed that the cell K^+ must be bound in some way or other. At the time, the only systems known with a very high binding selectivity were antibiotics such as nonactin and valinomycin. The structure responsible for their specificity is a «cage» of 6 – 8 carbonyl oxygen atoms arranged in space according to a definite pattern. If the same principle were to be responsible for K^+ binding in *H. marismortui*, 24 – 32 moles oxygen per litre of cell water would be required, enormous amounts of oxygen atoms that cannot be supplied exclusively by the organic components of the cell.

It is therefore suggested that the oxygen atoms required might be furnished by the ordering of water molecules forming a tertiary system of water, KCl and cell proteins.

Neutron scattering experiments were designed to examine intra-cellular water diffusion, following on previous work by Ginzburg and collaborators, using a variety of methods, on the cytosolic environments in the extreme halophile *Haloarcula marismortui* (*Hm*). The results revealed an extremely slow water component in *Hm*. Quasielastic Neutron Scattering (QENS) experiments were performed on the IN16 neutron spectrometer at ILL, on samples of fully deuterated *Hm* [3]. The BSS neutron spectrometer at FRJ-2 has about the same resolution then IN16. This spectrometer is therefore well adapted to examine whether this extremely slow water exists in *E. coli*.

Methods and results

Deuterated *E. coli* cell samples were prepared in collaboration with the Deuteration Laboratory of the Institut Laue Langevin and resuspended in H₂O or D₂O solutions. The two cell samples were named D-cells H₂O and D-cells D₂O, respectively. Sample holders were made of aluminum and measured 4 x 3 cm with a depth of 0.2mm. The quasielastic experiments were performed at 285K on the BSS backscattering spectrometer using an incident wavelength of 6.27 Å. The elastic energy resolution (FWHM) is 1.2 µeV corresponding to time scales of about 1 ns. The scattering was measured over a wave-vector range of $0.2 < Q < 1.9 \text{ Å}^{-1}$. All samples, including the vanadium calibration sample and empty aluminum can, were oriented at 45° with respect to the incident neutron beam direction. The vanadium sample (a purely elastic scatterer) was measured in order to define the instrument resolution and to correct for detector efficiency. The measured spectra were corrected, normalized, grouped, and transformed into energy transfer spectra. The spectra of the D-cells H₂O and D-cells D₂O samples are identical in all the Q range (Figure 1), demonstrating that the extremely slow cell structured water do not exist in *E. coli* cells. Thus, our data reinforce our hypothesis. The existence of the very slow water component in *H. marismortui* suggests a specific water structure, which would also be responsible for the large amounts of K⁺ ions found to be bound within these cells.

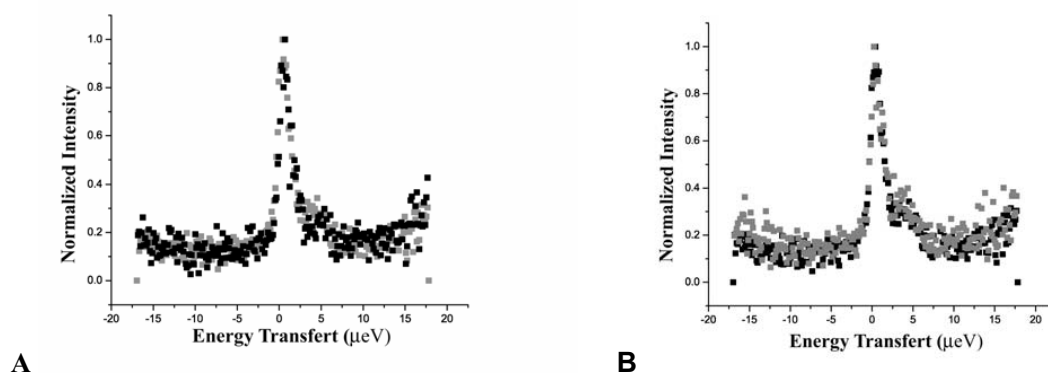


Figure1: Normalized quasielastic spectrum of D-cells H₂O (gray) and D-cells D₂O (black) at $Q = 0.31 \text{ Å}^{-1}$ (A) and $Q = 1.86 \text{ Å}^{-1}$ (B).

References

- (1) Egelstaff P.A. (1965) Thermal Neutron Scattering. Academic Press. London and New York.
- (2) Bellissent-Funel M. C., Teixeira J., Chen S. H., Dörner B., Middendorf H. D., Crespi H. L. (1989). Low-frequency collective modes in dry and hydrated proteins. *Biophys. J.* 56, 713-716.
- (3) Ginzburg, M., Sachs, L. & Ginzburg, B. Z. (1970) *J. Gen. Physiol.* **55**, 187-207.
- (4) Tehei M., Franzetti B., Wood K., Gabel F., Fabiani E., Jasnin M., Zamponi M., Oesterhelt D., Zaccari G., Ginzburg M., Ginzburg B.Z. (2006) Neutron scattering reveals extremely slow water in a Dead Sea organism. In revision for PNAS.



Experimental Report
of Neutron Scattering Experiments
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Proposal number:	BSS-05-006		
Experiment title:	Self motions of PMMA close and above the glass transition		
Dates of experiment:	16/05/2005-25/05/2005	Date of report: 11/10/2005	
Experimental team: Names	Addresses		
Caroline Genix Juan Colmenero Arantxa Arbe Dieter Richter	Donostia International Physics Center, Apdo. 1072, 20080 San Sebastian, SPAIN Dpto. de Física de Materiales, UPV/EHU, , “ , “ , “ Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ IFF, FZJ, Jülich, Germany		
Local Contact:	Andreas Wischnewski		

Experimental report text body

The aim of this experiment was to investigate the segmental relaxation in syndiotactic poly(methyl methacrylate) (PMMA) ($T_g=400K$) through the hydrogen motions. The sample studied was PMMA with deuterated ester-methyl group (PMMA d_3). In this way the spectra revealed the dynamics of the main-chain and α -methyl group hydrogens (see scheme), while the ester-methyl hydrogens were "hidden" for neutrons. The reason to avoid contributions from such atoms was that in a recent MD-simulations study the dynamics of the ester side group has been found to be significantly faster than that associated to the main chain [1].

The BSS measurements have been performed at 4, 300, 350, and each 25K between 400K and 525K.

The sample was placed in an Aluminum flat container at 45° with respect to the incident beam. The thicknesses were such that a transmission of ≈ 0.9 was calculated. With $\lambda=6.27\text{\AA}$ a Q-range of $0.16 \dots 1.87\text{\AA}^{-1}$ was accessed and an energy window of $\pm 17\mu\text{eV}$ was explored. Measuring times of about 20 hours were employed to achieve reasonable statistics, as can be appreciated in Fig. 1 (at 300K measurement we counted only for 7 hours). Vanadium and empty cell measurements were also carried out to correct the spectra.

From our last results obtained by BSS and MD-simulations on PMMA in a PEO/PMMA blend [1], we expected that below 400K the quasielastic broadening of the PMMA d_3 spectra could only relate to the α -methyl group rotation in the BSS window. The quantitative analysis of the spectra at 300K, 350K and 400K by using this approach delivers a good description of the experimental data and allows determining the characteristic timescale for this rotation. The results [see Fig. 2(a)] are in good agreement with those obtained in [1] for PMMA in the blend, corroborating the hypothesis that blending does not affect such localized motions.

Above 400K, additional broadening is observed that should be attributed to the segmental relaxation. We described such contribution by the Fourier transform of a stretched exponential function, $\exp[-(t/\tau)^\beta]$. In the fitting procedure, the values of the β parameter were fixed to those obtained from dielectric spectroscopy experiments on PMMA ($\beta = 0.3$ for 425K, 0.5 for 450K and 0.56 for higher temperatures). The α -methyl group rotation was taken into account by construction of an "effective resolution" including the quasielastic broadening expected from this motion properly weighed by the relative abundance of such atoms and the appropriated EISF. Assuming statistically independent rotation and segmental relaxation, the global dynamics is described by the convolution of both functions. Very satisfactory fits are achieved, as can be seen in Fig. 1. Moreover, the characteristic times obtained at $Q = 1 \text{ \AA}^{-1}$ for segmental dynamics of PMMA are in a good agreement with dielectric spectroscopy results [see Fig. 2(a)]. Finally, Fig. 2(b) shows the Q -dependence of the characteristic times obtained for the α -relaxation. Weaker dependences with respect to that expected in the Gaussian approximation [$\propto Q^{-2/\beta}$] are found. This might be a consequence of the heterogeneous dynamics developed by the different hydrogens in the sample.

References:

[1] A.-C. Genix, A. Arbe, F. Alvarez, J. Colmenero, L. Willner, D. Richter, PRE **72**, 31808 (2005)

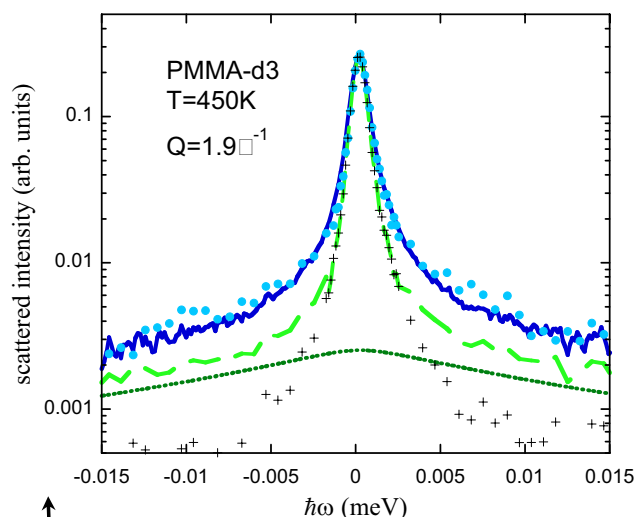


Fig. 1: Scattering function measured at $Q = 1.9 \text{ \AA}^{-1}$ and 450 K for PMMA-d3. The solid line is a fitting curve consisting of a KWW function to describe the overall segmental dynamics convoluted with an effective resolution (dashed line) giving account for the α -methyl group rotations. The quasielastic component of the α -methyl group rotations is depicted by the dotted line. The resolution function is shown by the crosses.

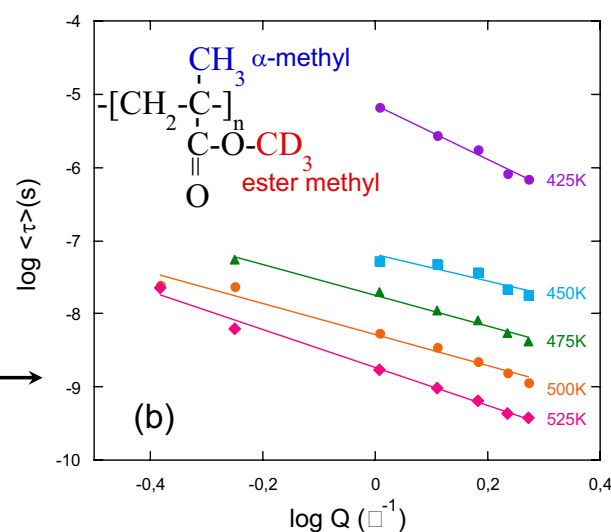
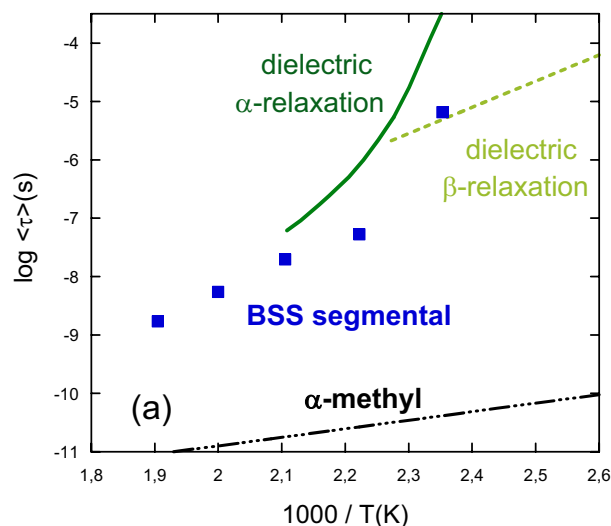


Fig. 2: Characteristic times for segmental motion of PMMA. (a) Temperature dependence for $Q = 1 \text{ \AA}^{-1}$; (b) Momentum transfer dependence for the temperatures investigated



Experimental Report
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Proposal number:	BSS-05-007		
Experiment title:	Elastic fixed window scan of glass-forming propyleneglycol		
Dates of experiment:	11.–13.04.2005	Date of report:	19.05.2005
Experimental team: Names	Addresses		
Maria Mayorova Andreas Wischnewski Reiner Zorn	IFF, FZ Jülich IFF, FZ Jülich IFF, FZ Jülich		
Local Contact:	Andreas Wischnewski		

Experimental report text body

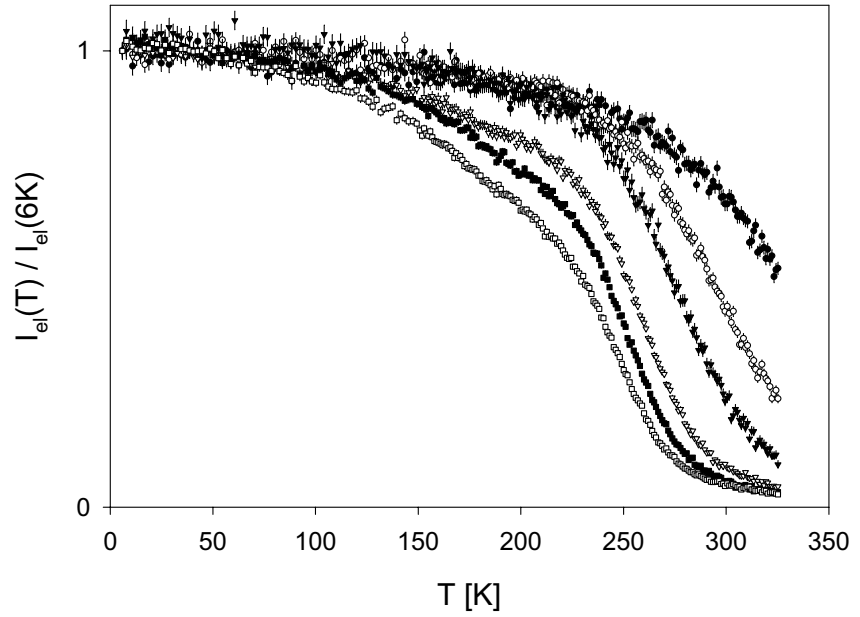
This is a preparatory experiment for future inelastic neutron scattering experiments on a microemulsion containing propyleneglycol (PG) as nanoscopic droplets. Details of the system are described in ref. 1. The special interest for this microemulsion arises from the fact that one can observe the glass transition of the inner micro-phase (PG) separately and thus study the confinement effect on the glass transition.

Here we performed an elastic fixed window scan on the *bulk* reference. Previous work has shown that this is often not a trivial task because of the tendency of low-molecular liquids to crystallise. The experiment was done using a hollow cylindrical aluminium sample holder with anodised surfaces. The sample was quenched in liquid nitrogen and an up-scan from 2 K to 325 K was done. If crystallisation would have occurred this could be clearly seen from an abrupt increase of elastic intensity. Experiments on IN16 with its diffraction detector in parallel have shown that, surprisingly, this criterion is even clearer than the occurrence of Bragg peaks (in predominantly incoherently scattering samples).

Subtraction of the empty container and corrections for self-shielding were done by the ILL program SQWel adapted to the Jülich BSS data format.

As Fig. 1 shows the elastic scans do not show any such signature of crystallisation. Instead, the intensity decreases monotonously with temperature. This proves that the given construction of the sample holder can be used in future experiments over the whole temperature region without taking the risk of crystallisation during the measuring time.

Fig. 1: Elastic scans of propyleneglycol: intensities normalised to 5.9 K. Q values: ● 0.20 Å⁻¹, ○ 0.37 Å⁻¹, ▼ 0.56 Å⁻¹, ▽ 1.02 Å⁻¹, ■ 1.41 Å⁻¹, □ 1.80 Å⁻¹.



From the elastic scans mean-square displacements $\langle u^2 \rangle$ of the scatterers (predominantly protons) were calculated using the cumulant expression

$$I_{\text{el}}(Q) \propto \exp \left(-\frac{\langle u^2 \rangle}{3} Q^2 + \frac{A \langle u^2 \rangle^2}{72} Q^4 \right).$$

Fig. 2 shows the result. (The non-Gaussianity parameter A was not extracted because it contains also the multiple scattering effects.) The mean-square displacement shows the characteristic behaviour for glass-forming materials. At low temperatures it is roughly proportional to temperature, at intermediate temperatures it increases more strongly due to fast processes, and above $T_g = 167$ K a strong increase due to the α relaxation sets in. What is remarkable is that the methyl group rotation is not visible. From measurements on polymers containing methyl groups it is expected to show up as a step in the mean-square displacement at about 120 K with an amplitude $3/8 \langle u^2 \rangle_{\text{CH}_3} = 0.38 \text{ Å}^2$. If at all it takes place at a higher temperature indicating that the barrier height for methyl-group rotation is larger than in other substances.

[1] Lin-Min Wang, Fang He, R. Richert, *Phys. Rev. Lett.* **92**, 095701 (2004)

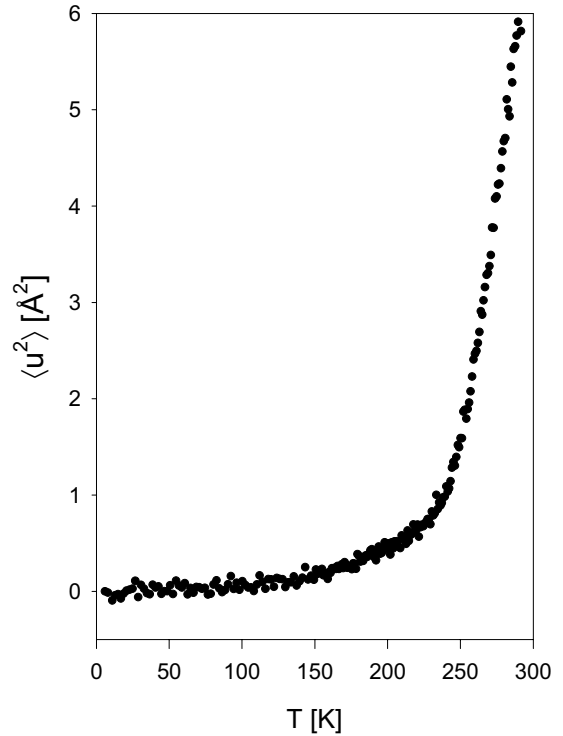


Fig. 2: Mean-square displacement of protons in propyleneglycol at the characteristic time corresponding to the resolution of the Jülich BSS spectrometer (≈ 2 ns)



Experimental Report
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Proposal number:	BSS-05-008		
Experiment title:	Concentration dependence of PEO dynamics in a blend of PEO/PMMA		
Dates of experiment:	25.05 – 29.05.2005 06.06 – 07.06.2005 15.06 – 21.06.2005	Date of report:	28.11.2005
Experimental team: Names	Addresses		
Katarzyna Niedzwiedz	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Andreas Wischnewski	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Michael Monkenbusch	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Andreas Wischnewski Dr. Michaela Zamponi		

Experimental report text body

Although it is well known for a long time that the dynamics of each component of a binary polymer mixture is affected by blending, the dynamic miscibility and in particular the question whether or not there exists a corresponding length scale is still matter of strong controversy [1]. The unsolved problem of how local friction arises in chemically heterogeneous environments makes it impossible to predict the properties of a blend system on basis of what is known about the behaviour of each component of the mixture.

Of particular interest are blends where the dynamics of the pure components are well separated in time, i.e. with a very different glass transition temperature T_g of the components. In this case the slow (high T_g) ingredient forms a stiff network within the faster (low T_g) component.

In this experiment we investigated the miscible PEO / PMMA blend ($T_g^{\text{PEO}} \approx 210 \text{ K}$, $T_g^{\text{PMMA}} \approx 400 \text{ K}$) with two different compositions: 35 % PEO / 65 % PMMA and 50 % PEO / 50% PMMA.

Since we were interested in the motion of the faster component (PEO) blends with protonated PEO and deuterated PMMA were measured. The data were corrected for background (the intensity coming from an empty cell was measured separately) and the instrument resolution was determined by measuring the blend sample at $T=4 \text{ K}$.

Preliminary treating of the data shows changes in the PEO dynamics for the different samples. Figures 1 –3 illustrate the dynamic structure factor for the different compositions of the PEO / PMMA blend. One can see that with increasing PEO concentration the intensity decreases and the spectra become broader, i.e. the quasielastic scattering is more pronounced as it is found for increasing Q-values or temperatures.

A full evaluation of the data is still going on. For a quantitative description one in particular needs to account for the elastic contribution to the signal from coherent scattering.

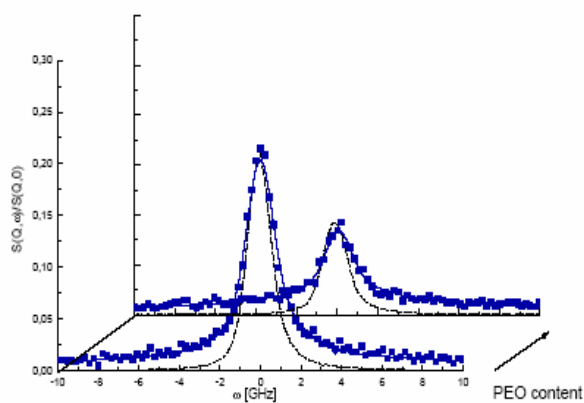


Fig. 1 Neutron scattering spectra of a PEO/PMMA blend with different concentrations: 35%PEO / 65%PMMA and 50% PEO / 50% PMMA at $T = 375$ K and $Q = 1.017 \text{ \AA}^{-1}$. The dashed lines show the instrument resolution (blend at $T = 4$ K), the solid lines represent fits with the Kohlrausch-Williams-Watts (KWW) function for a stretching parameter $\beta = 0.5$.

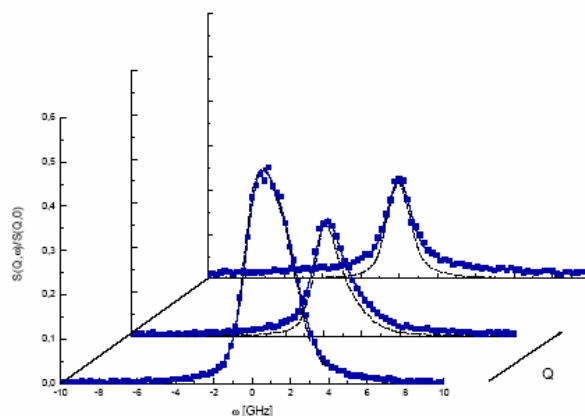


Fig. 2 Neutron scattering spectra of a blend with 35% PEO and 65% PMMA at $T = 350$ K and different Q values: $1.287, 0.564$ and $0.242 \text{ \AA}^{-1}$. The dashed lines show the instrument resolution, the solid lines represent fits with the KWW function for $\beta = 0.5$.

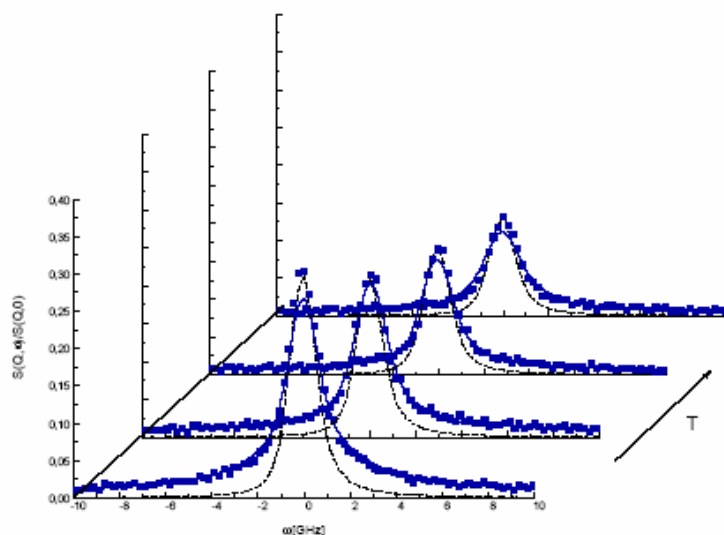


Fig. 3 Neutron scattering spectra for a blend with 35% PEO and 65% PMMA in a temperature range between 350 K and 425 K in steps of 25 K at $Q = 1.017 \text{ \AA}^{-1}$. The dashed lines show the instrument resolution, the solid lines represent fits with the KWW function for $\beta = 0.5$.

[1] S. Hoffman et al., Physical Review Letters 85, 772 (2000)



Experimental Report
of Neutron Scattering Experiments
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Proposal number:	BSS-05-009		
Experiment title:	Elastic fixed window scan of a glass forming microemulsion		
Dates of experiment:	07–15.06.2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Zorn, Reiner Mayorova, Maria	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Andreas Wischnewski, Michaela Zamponi		

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The effect of the soft confinement (microemulsion) on the microscopic dynamics of the glass-forming liquid Propylene Glycol (PG) with $T_g=167$ K was investigated. For this purpose a three component microemulsion was chosen: propylene glycol as investigated material which was enclosed within the inversed micelles, AOT – ionic surfactant for system stabilization, decalin as oil phase ($T_g=135$ K). In such a system investigated the glass-forming liquid is surrounded with a more fluid environment near its T_g . Dielectric spectroscopy revealed an acceleration of PG dynamics close to T_g compared to the bulk (confinement effect) and 7K shift of its T_g to lower value [1]. The incoherent neutron elastic spectra measurements were done with the PI spectrometer (wave length of $\lambda=6,30$ Å) on PG confined in reversed micelles (averaged radius about 8,5 Å) and pure PG. To extract information concerning confined PG data obtained for a completely deuterated microemulsion were subtracted from data for a microemulsion with protonated PG and deuterated other components.

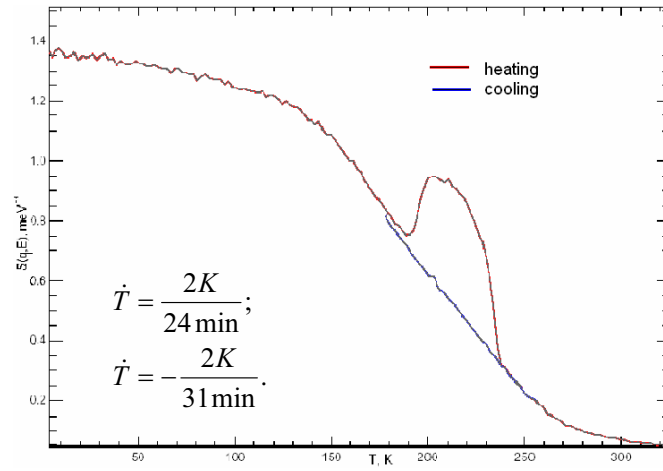


Fig.1. Confined PG elastic spectra.

As one can conclude from Fig.1 there is temperature range of crystallization of confined PG for the heating branch which was previously not detected because this temperature range was not studied (Fig. 1). So to avoid this crystallization cooling branch should be chosen.

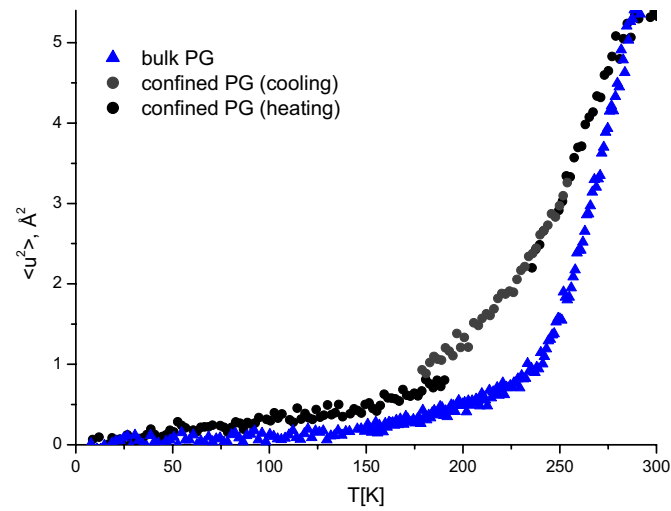


Fig. 2. Mean square displacement.

The information about mean square displacement was extracted from a cumulant expansion of the incoherent scattering function. From comparison results for bulk and confined PG it can be concluded that there is shift of glass transition temperature to lower temperature range (Fig. 2).



Experimental Report
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Proposal number:	BSS-05-010		
Experiment title:	Influence of the matrix on the confinement effect in polymer blends close to the glass transition		
Dates of experiment:	24/10/2005-06/11/2005	Date of report:	29/05/2006
Experimental team: Names	Addresses		
Anne-Caroline Genix Arantxa Arbe Juan Colmenero Andreas Wischnewski Dieter Richter	Donostia International Physics Center, Apdo. 1072, 20080 San Sebastián, SPAIN Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ Dpto. de Física de Materiales, UPV/EHU, , “ , “ , “ IFF, FZJ, Jülich, GERMANY IFF, FZJ, Jülich, GERMANY		
Local Contact:	Andreas Wischnewski (BSS), Werner Schweika (DNS)		

Experimental report text body

Currently, a big deal of activity in polymer research is focused on the question of the dynamic miscibility, i.e., how the dynamics of each component in a miscible blend are affected by blending. Particularly interesting are blends of components with very different glass-transition temperature, T_g , as poly(ethylene oxide) / poly(methyl methacrylate) (PEO/PMMA) [PEO: $T_g=214K$, PMMA: $T_g=400K$]. In a very recent backscattering experiment [1], the space/time resolution and selectivity (H/D) of neutron scattering allowed us to directly observe the confined and heterogeneous nature of the molecular motions of PEO in the blend. It lead to the following scenario: at temperatures close to the blend T_g , the presence of the hardly moving PMMA matrix leads to the creation of little pockets of mobility where PEO can move [1]. However, this confinement effect - consequence of a non-equilibrium situation - still deserves a deep scrutiny. In this experiment we have chosen to focus on the influence of the matrix on the confinement effect.

The system investigated was poly(ethylene oxide) / polyethersulfone (PEO/PESF), where the difference between the T_g 's for each of the pure components is of the order of 260K (PESF: $T_g=476K$). By backscattering we wanted to follow the scattering dominated by the incoherent contribution of the hydrogens of the protonated (h) PEO component in the blend, where the other component is deuterated (d), and compare these results with those previously obtained for the PEO in a blend with PMMA [1] and in a blend with poly(vinyl acetate) (PVAc) [2]. The BSS measurements have been performed on the following samples: pure PESF (deuterated) at 4, 250, and 400K, and a blend of hPEO/dPESF (25%/75%) at 4, 250, 270, 290, 350, 375 and 400K. This corresponds to the region well above the glass transition for PEO but close to or below that of PESF. The samples were placed in Aluminum flat containers at 45° with respect to the incident beam. The

thicknesses were such that a transmission of ≈ 0.9 was calculated. With $\lambda=6.27\text{\AA}$ a Q-range of $0.16 \dots 1.87\text{\AA}^{-1}$ was accessed and an energy window of $\pm 17\mu\text{eV}$ was explored. Reasonable statistics was achieved with measuring times of about 30 hours. Vanadium and empty cell measurements were carried out to correct the spectra. For $Q=1\text{\AA}^{-1}$, Fig. 1 shows the spectra corresponding to PEO pure [1] and in the blend at 350 K. A clear slowing down in the dynamics of PEO is observed as effect of blending.

In addition, we used the diffuse scattering spectrometer (DNS) in its diffraction mode, in order to determine the Q-dependence of the relative amount of the coherent contribution to scattering of the samples. λ was set to $3.3\text{\AA}$ enabling a Q-range up to $3.36\text{\AA}^{-1}$. The samples were placed into a hollow cylinder and in Aluminum flat container, for the blend and the pure PESF, respectively. The blend was measured at the same temperatures investigated by BSS (with exception of the measurement at 20K) and the pure PESF at room temperature only. Measuring times of one hour were employed. Measurements of NiCr, Vanadium and both empty sample-holders were also carried out to correct the experimental data. We realized from these diffraction measurements (see Fig. 2) that the deuteration level of the PESF sample was not as high as expected. This implies that incoherent contributions coming from the PESF component in the blend will have to be also taken into account. A quantitative analysis of the BSS spectra in terms of a log-normal distribution of relaxation times is currently being performed.

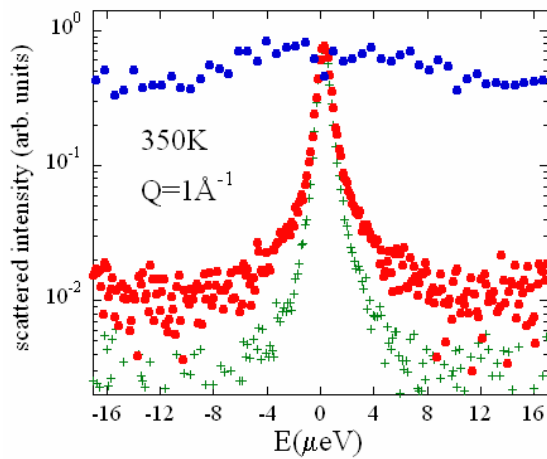


Fig. 1: Scattering function measured at $1\text{\AA}^{-1}$ and 350 K for pure PEO (protonated) (blue circles) [1] and the blend containing 25% of protonated PEO in a deuterated PESF matrix (red circles symbols). The functions are normalized to their maximum intensities. The resolution function is displayed by the crosses.

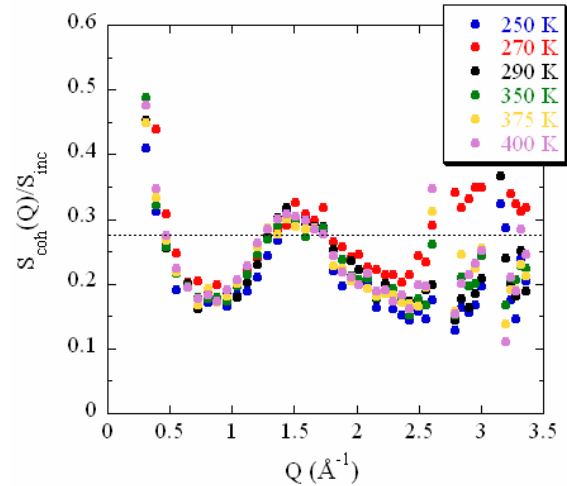


Fig. 2: Ratio between the coherent and incoherent scattering intensities measured by means of DNS at several temperatures for the blend hPEO/dPESF (25%/75%). The dotted line indicates the expected level for the same blend but with fully deuterated PESF component.

References:

- [1] C. Genix et al., Experimental Report FZJ: BSS-04-019; A.-C. Genix et al., Phys. Rev. E 2005, 72, 031808.
- [2] M. Tyagi et al., Macromolecules 2006, 39, 3007.



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

Proposal number:	BSS-05-011		
Experiment title:	Rotational dynamics of methyl groups in di-amino-durene		
Dates of experiment:	2.7.2005 – 9.7.2005	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
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Local Contact:	H. Grimm		

Experimental report text body

A study of charge transfer complex diaminodurene(DAD):tetracyanoquinodimethane (TCNQ) with the methylated benzene derivative DAD (Fig.1) as electron donor and TCNQ as acceptor molecule is complemented by a study of the pure donor compound to get a starting point for the discussion of steric and charge changes in the molecular complex. While the methyl groups of DAD in TCNQ show no tunnelling, pure DAD does. An improved energy resolution of the backscattering spectrometer BSS1 is obtained in the present experiment compared to the previous one [1] by using the standard centered setup with the unpolished Si[111] monochromator: $\delta E = 1.1 \mu\text{eV}$. This allows to resolve the previously observed inelastic bands.

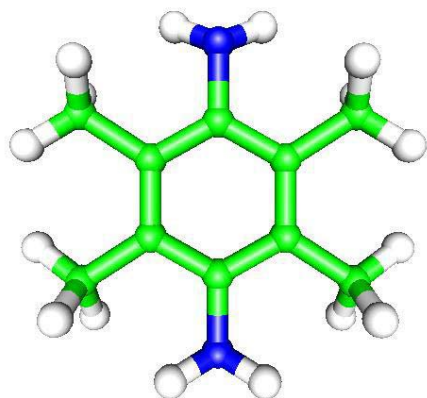


Fig.1 Schematic view of diaminodurene molecule.

The figure 2 compares the spectrum of DAD taken at a sample temperature $T=4.5\text{K}$ with the resolution function of the spectrometer. The presence of 3 tunnelling transitions is visible and confirmed by a fit procedure. The three tunnelling transitions at energies 1.5, 4.0 and $6.5\mu\text{eV}$ show relative intensities are 2:1:1 compared to an elastic intensity of 35. The inner line was not seen in the previous experiment. The band intensities can be interpreted with respect to structural properties. If we assume that all tunnel splittings are resolved and allow for some spurious elastic intensity from Bragg reflections etc we can conclude that the unit cell of DAD contains a single type of molecules at a site of no symmetry.

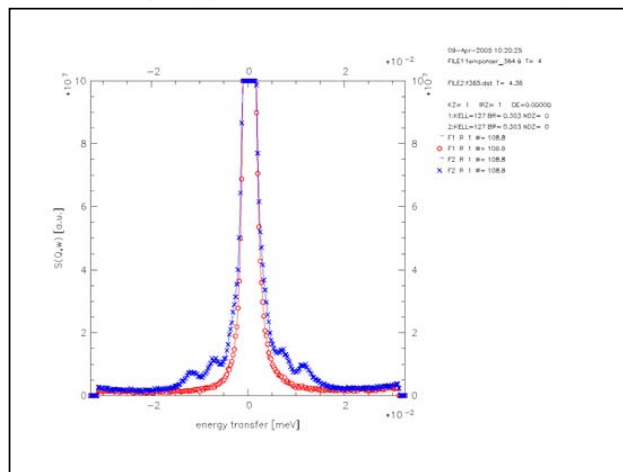


Fig.2 Spectrum of diaminodurene (xxx) in the μeV range. Sample temperature $T=4.5\text{K}$. Resolution function (ooo) for comparison

[1] Experimental reports FRJ2 2004, BSS-04-003



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

Proposal number:	BSS-05-012		
Experiment title:	Effect of solvents on dynamics of a β -lactoglobulin protein		
Dates of experiment:	18-29, August, 2005	Date of report:	1 March, 2006
Experimental team: Names	Addresses		
BELLISSENT-FUNEL, Marie-Claire	Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay 91191 Gif-sur-Yvette cedex, FRANCE		
YOSHIDA, Koji	Laboratoire Léon Brillouin (CEA-CNRS), CEA-Saclay 91191 Gif-sur-Yvette cedex, FRANCE		
Local Contact:	Dr. Andreas Wischnewski		
<u>Experimental report text body</u>			

Solvent plays an important role in the protein folding. Alcohol, which is one of them, has the capability to increase the content of secondary structure (α -helix) in proteins and to denaturate the protein. In the present experiment, in order to observe the solvent effect on protein dynamics, inelastic neutron scattering of β -LG (BLG) with adsorbed H_2O , D_2O , ethanol, and deuterated ethanol (4 samples) were measured with High Resolution Backscattering Spectrometer (BSS). Amount of adsorbed solvents for all samples is 0.5 g per g of dry protein. The Q values for each sample are ranging from 1.6 to 18.2 nm^{-1} . Temperatures measured are 280 K and 298 K. Measuring time was 24 hours per spectrum. In addition, we measured an empty can and a vanadium plate for resolution measurement. (The energy resolution is 1.3 ~ 1.8 μeV .)

Figure 1 shows some typical dynamical structure factors at $Q = 9.7 \text{ nm}^{-1}$. The peak intensities of samples were normalized to that of vanadium spectra. The quasielastic peaks of both H_2O -BLG and ethanol-h-BLG are clearly shown in the Figure 1 (a). These spectra contain both contributions from surface water (or ethanol) molecules and protein. Although some features of hydrated protein dynamics from sub-picosecond to nanosecond were previously revealed by elastic, quasielastic, and inelastic incoherent neutron-scattering measurements [1], the present results revealed that such a slow dynamics of protein exists in ethanol as well as in water. The relaxation of surface water molecule and protein in H_2O -BLG is faster than that of ethanol molecule and protein in ethanol-h-BLG. Previously, we measured water and ethanol adsorbed BLG with the zero-field spin echo spectrometer located at reactor Orphée of LLB and investigated the intermediate incoherent scattering functions $I(Q, t)$ at $Q = 8 - 18 \text{ nm}^{-1}$. A relatively slow relaxation was found, implying the

existence of a slow dynamics of both protein and surface solvents. The present results look in agreement with the NSE results. From the difference between the quasielastic spectra shown in Fig.1 (b), we will deduce the dynamic properties of surface water [2]. The same information can be obtained for surface ethanol from Fig. 1 (c). Fig 1 (d) exhibits some tiny differences between dynamics of BLG respectively in D₂O and ethanol-d. There is same tendency for dynamics of BLG protein in D₂O to be faster than in ethanol-d. It is consistent with MD simulation results that a small peptide (melittin) in pure water takes more various conformations than in alcohol-water mixture [3].

The present results will allow us to access the local site dynamics of the protein depending on the solvents. This dynamic information will give us important hints to understand the role and underlying mechanism of solvents such as water and alcohols in protein folding. The further analysis is in progress.

References

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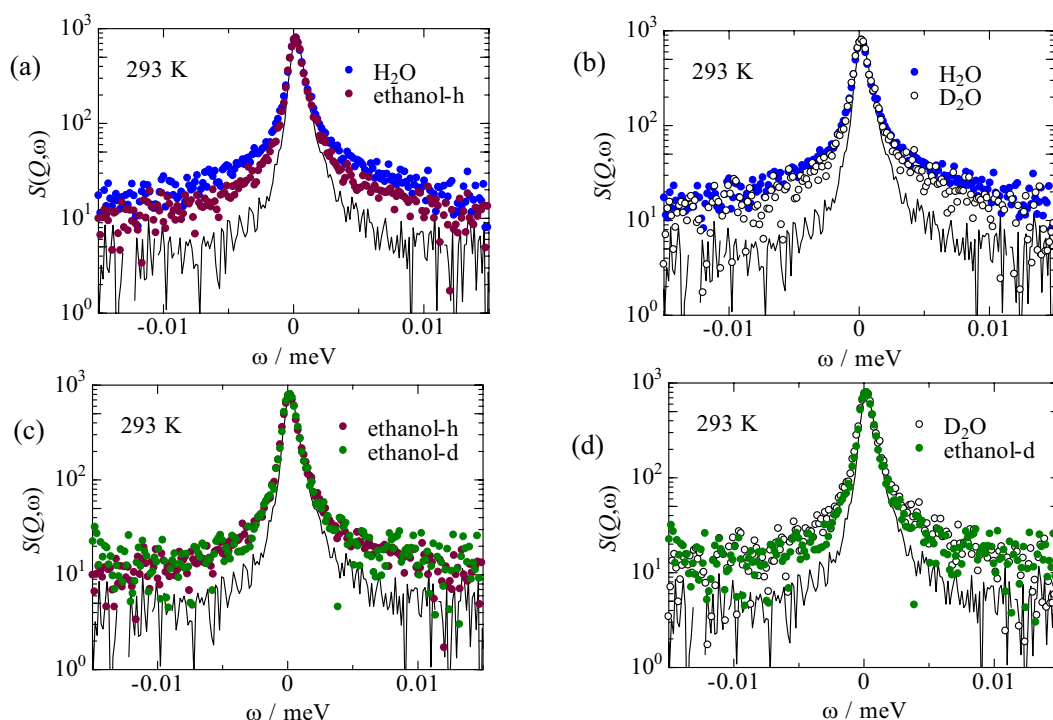


Fig.1. Dynamical structure factors of water and ethanol adsorbed BLG powder at $Q = 9.7 \text{ nm}^{-1}$. The solid lines indicate the resolution function. The peak intensities of samples are normalized to that of vanadium spectra. (a) H₂O-BLG and ethanol-h-BLG at 293 K, (b) H₂O-BLG and D₂O-BLG at 293 K, (c) ethanol-h-BLG and ethanol-d-BLG at 293 K, and (d) D₂O-BLG and ethanol-d-BLG at 293 K.



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

Proposal number:	BSS-05-016		
Experiment title:	Extraction of radial and longitudinal dynamics of nano-alumina confined polymer electrolytes.		
Dates of experiment:	12/12/2005 to 19/12/2005	Date of report:	13/01/2006
Experimental team: Names	Addresses		
Karine Lagrené Jean-Marc Zanotti	Laboratoire Léon Brillouin (CEA-CNRS) C.E.A Saclay 91191 Gif-sur-Yvette Cedex France		
Local Contact:	Dr. Michaela Zamponi		

Experimental report text body

Introduction

Porous alumina membranes (AAO) are macroscopically highly ordered nano-confining systems made of oriented parallel cylindrical channels. The “average out” of dynamical information occurring in isotropic confining systems can be then overcome by proper relative orientation of the AAO pore axes relative to the beam. The objective of the experiment was to extract the radial and longitudinal dynamical effect of confinement on hydrogenated PEO.

Experimental

The PEO used in the present study was hydrogenated PEO (molecular weight = 600,000 g/mol, Aldrich). A 0.2 ± 0.05 mm thickness PEO film was prepared by melting under vacuum at 95°C the needed amount of PEO directly into the neutron measuring cell (total polymer mass 430 mg).

Porous alumina membranes (AAO) are macroscopically highly ordered nano-confining systems made of oriented -tens of microm long- parallel cylindrical channels. MEB image of such a LLB custom made AAO membrane show that the average pore radius is 20 nm. A single membrane is a 1 cm² single plate.

Confined samples were prepared by melting, under vacuum at 95°C, onto porous alumina membranes AAO membranes hydrogenated PEO 600000 g/mol. height such membranes filled with polymer were prepared. We estimate the total mass in the beam to be about 40 mg.

A quick test SANS experiment has been performed on the KWS-1 spectrometer (courtesy Dr. Pyckhout-Hinsén) on empty and full AAO membranes. Based on a contrast argument we are confident that the membranes pores were filled by the polymer.

Using BSS, an elastic scan has been performed on both the bulk and confined samples. As seen from figures 2 and 3, the melting temperature of the confined polymer is reduced by 10 degree compared to the bulk. These results are in agreement with previous DSC measurement (Figure 4), confirming a striking confinement effect.

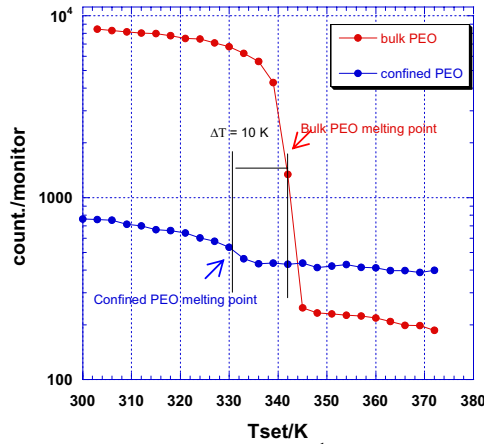


Figure 1: Elastic scans ($Q=1.28 \text{ Å}^{-1}$) performed on bulk PEO and confined PEO from 300 K to 373 K.

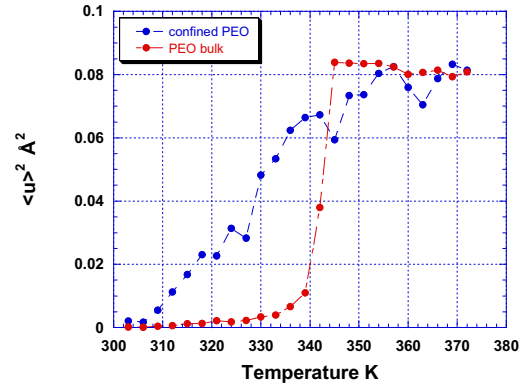


Figure 2: Temperature dependence of the mean square displacement $\langle u^2 \rangle$ for the bulk and confined PEO.

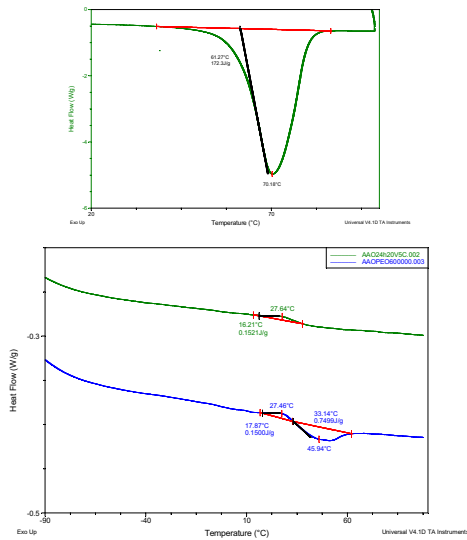


Figure 3: DSC measurement for bulk (top) and confined PEO (blue curve bottom plot, empty AAO membrane is the green curve).

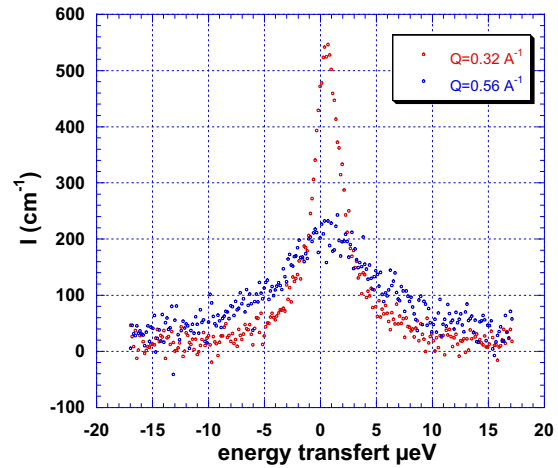


Figure 4: Bulk PEO $S(Q, \omega)$ at $T = 373 \text{ K}$.

Scattering was nevertheless too weak to perform inelastic scans on the confined polymer above the melting point (see relative intensities Fig.1). We have therefore performed a full inelastic measurement on the bulk sample (Figure 4).

To obtain excellent statistics, this measurement has been performed at a single temperature (373 K) so as to test a new model (describing bulk PEO dynamics) under development in our team.



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

Proposal number:	BSS-05-017		
Experiment title:	Isotropic spin relaxation in hematite (α-Fe₂O₃) nanoparticles		
Dates of experiment:	28.09. - 07.10. 2005	Date of report:	17. 10. 2005
Experimental team: Names	Addresses		
Christian R. H. Bahl	Materials Research Department, AFM-228 Risø National Laboratory Frederiksborgvej 399 DK-4000 Roskilde Denmark		
Luise Theil Kuhn (Dr.)			
Hjalte Sylvest Jacobsen			
Local Contact:	Andreas Wischniewski		

Experimental report text body

The present experiment is a continuation of experiment number BSS-04-023. Here the spontaneous reversal of the magnetisation due to thermal effects, so-called superparamagnetism, was studied in hematite nanoparticles. To samples of 8 nm nanoparticles of the canted antiferromagnet hematite (α -Fe₂O₃) were studied, one as-prepared, where there is a strong interparticle (exchange) interaction, and one where the particles have been individually coated with phosphate thus reducing these interactions significantly. In the present work the study of these two samples was continued. The aim was to study the phenomenon of isotropic relaxation of the spins, which is predicted to occur when the time scale of superparamagnetism and collective magnetic excitations becomes similar. Collective magnetic excitations are coherent precessions of the spins around the easy axis of magnetisation.

Isotropic relaxation is predicted to be observed as a large reduction in the scattering signal from a magnetic Bragg reflection. Elastic temperature scans of the sample of the strongly interacting particles are presented in Figure 1. As can be seen, the intensity decreases in all of the detector channels, probably due to water bound to the surface of the particles. However, the signal in the channels recording magnetic Bragg peaks ($q=1.52\text{\AA}^{-1}$ and $q=1.28$, Bragg peaks at $q=1.51\text{\AA}^{-1}$ and $1.37\text{\AA}^{-1}$) decreases fastest. Normalising these signals by the signal from the structural reflection ($q=1.72\text{\AA}^{-1}$, Bragg peak at $q=1.70\text{\AA}^{-1}$) gives the data in Figure 2. The solid green line is from data recorded previously on the weakly interacting sample. This displays a very rapid decrease of intensity around 50 K. The data from the sample of strongly interacting particles has a gradual decrease at low temperatures, becoming more rapid at higher temperatures, as illustrated by the two black line segments as guides to the eye. The initial slow decrease can be ascribed to the decrease in the average magnitude of the spins caused by the increasing opening angles of the collective precessions with temperature. The Néel temperature is at around 950 K, so there is no significant decrease in the magnetisation due to temperature.

The later onset of isotropic relaxation and less dramatic decrease was expected in the sample of strongly interacting particles, as the interactions will lead to a broad distribution of timescales for the spin dynamics.

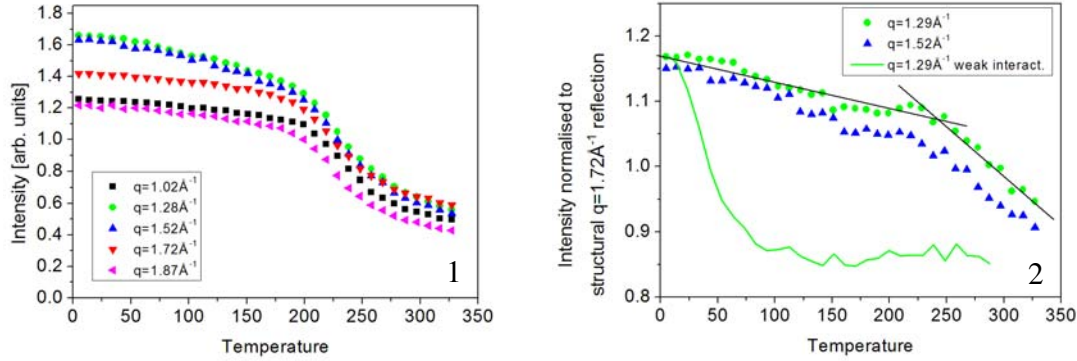


Figure 1: Elastic intensity from five of the detector channels. The detectors centred around $q=1.28 \text{ \AA}^{-1}$ and $q=1.52 \text{ \AA}^{-1}$ record antiferromagnetic reflections at $q=1.37 \text{ \AA}^{-1}$ and $q=1.51 \text{ \AA}^{-1}$ and the detector centred at $q=1.72 \text{ \AA}^{-1}$ records the structural reflection at $q=1.71 \text{ \AA}^{-1}$. The detectors centred at $q=1.02 \text{ \AA}^{-1}$ and $q=1.87 \text{ \AA}^{-1}$ measure background q - values. The decrease of the magnetic reflections with temperature is seen, but it is difficult to quantify it, as the intensity in all the channels drops.

Figure 2: Comparison of the elastic signals for the strongly interacting particles ($\blacktriangle$ and $\bullet$) and the weakly interacting particles (solid line), normalised to the signal from the structural reflection at $q=1.72 \text{ \AA}^{-1}$. The line segments are guides to the eye, illustrating the two rates of decrease.

The areas and widths of the quasi-elastic peaks from the superparamagnetic signals are fitted with a Lorentzian line shape. As this Lorentzian signal is quite weak, great care should be taken when fitting. Some preliminary parameters of the fitted Lorentzian are presented in Figure 3 as solid symbols. The open symbols are the fitted parameters from the previous experiment. It is clearly seen how the width and area of the quasi-elastic Lorentzian grow exponentially in the sample of weakly interacting particles, before gradually decreasing. In the sample of strongly interacting particles, the increase is slower and the area only saturates, but does not decrease at the measured temperatures.

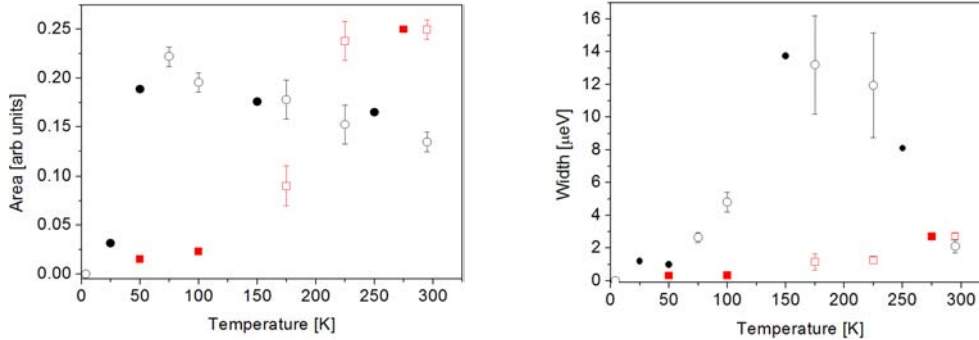


Figure 3: The width and area of the quasielastic Lorentzian, due to superparamagnetism. The graphs show the data from the sample of weakly interacting particles ($\bullet$ and $\circ$) and data from the sample of strongly interacting particles ($\blacksquare$ and $\square$). The closed symbols are preliminary fits to the data from the present experiment, while the open symbols display the data from the previous experiment.

In conclusion, we have shown that the relaxation of spins in hematite nanoparticles changes from a regime of superparamagnetism, to one of isotropic spin relaxation. In the strongly interacting particles, the onset of this transition is delayed, due to a larger and broader energy barrier. The interacting particles effectively act as one large particle.



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

Proposal number:	BSS-05-018		
Experiment title:	Effect on poly(ethylene oxide) dynamics of intercalation in sheet silicate		
Dates of experiment:	15.08 – 17.08.2005 29.08 – 02.09.2005 16.09 – 19.09.2005	Date of report:	02.03.2006
Experimental team: Names	Addresses		
Dr. Helen Hermes	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Henrich Frielinghaus	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Wim Pyckhout-Hintzen	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Andreas Wischniewski	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Andreas Wischniewski		

Experimental report text body

Polymer-clay nanocomposites have been found to exhibit enhanced mechanical and fire-retardant properties. Often, the clay must be organically “modified” to facilitate mixing with apolar polymers. To minimise the number of variables, we concentrate on a system in which the polymer interacts favourably with the clay without the need for such modification, i.e. the polyethylene oxide-montmorillonite system. Montmorillonite (MMT) is a naturally occurring layered silicate clay. In the dry state the individual platelet-like clay sheets which are about 1nm thick are stacked. A sandwich structure is formed if polymer intercalates between these platelets. To date, studies of polymer-clay composites and clay dispersions have been mainly limited to structural studies using small angle x-ray scattering. It is expected that studying the effect of confinement on the polymer chains and relating this to the enhanced mechanical properties observed will lead to an understanding of the behaviour of nanocomposites in general.

We have recently used solution intercalation to prepare composites of poly(ethylene oxide) (PEO) and sodium montmorillonite. Initial small angle neutron scattering experiments have been performed and the data described successfully¹. X-ray scattering and differential scanning calorimetry measurements have confirmed that using this sample preparation method and a suitable composition, it is possible for all the PEO to be intercalated between the silicate layers. The thickness of the intercalated PEO layers is 0.815 nm and extremely constant. Thus, this system is ideal for investigating the effect of extreme confinement on the dynamics (and conformation) of PEO polymer chains.

In the literature, nuclear magnetic resonance has been used to investigate similar samples on the local scale². Molecular dynamic simulations over the temperature range 273-423 K have been compared with these results and suggest that contrary to what might be expected, the confined polymer chains are less well ordered than in the bulk³.

This BSS experiment on a system with 20% PEO (fully protonated) / 80 % MMT was a feasibility study to test whether the segmental dynamics of these two-dimensional PEO chains are accessible by backscattering.

Fig. 1 compares spectra at T=375 K and T=425 K with the resolution (sample at T= 4 K). A temperature dependent broadening is clearly visible. This illustrates that the dynamics are within the energy window of the BSS spectrometer. An extensive quantitative evaluation of the data is on-going.

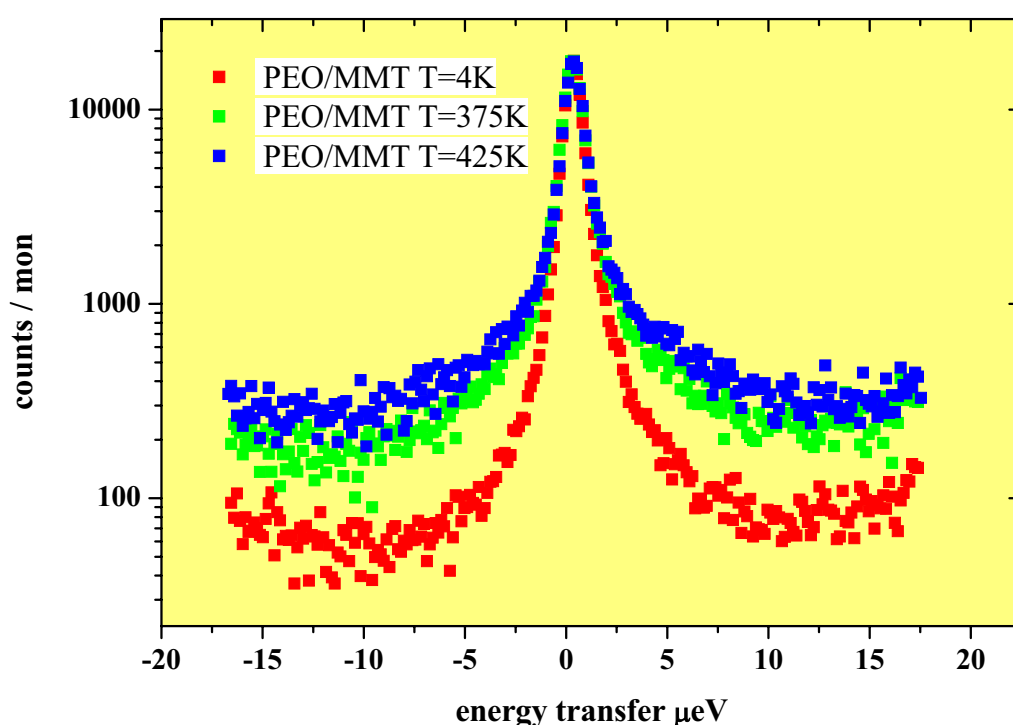


Fig.1: BSS spectra of 20% protonated PEO in MMT for T = 4K (resolution), 375 K and 425 K for $Q = 1.7 \text{ \AA}^{-1}$. The data are normalized to the same peak height.

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

Proposal number:	BSS-05-021		
Experiment title:	Isomerism and methyl rotational potentials of xanthines containing two methyl groups		
Dates of experiment:	1.12.2005, 4 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Forschungszentrum Jülich		
Local Contact:	M. Prager		

Experimental report text body

The methylxanthines represent a biologically most important class of molecules. These rather simple double ring molecules include the natural drugs caffeine, theobromine and theophylline which are used in daily live and medical application.

Caffeine is an alkaloid found in such foods as coffee fruit, tea etc. Its main pharmacological properties are a stimulant action on the central nervous system with psychotropic effects and stimulation of respiration, a stimulation of the heart rate. By oxidative demethylation caffeine is metabolized in the liver to the dimethylxanthines theobromine, theophylline and paraxanthine. In a second step demethylation leads to monomethylxanthines. Other metabolic steps follow. Theobromine is an alkaloid found in cocoa and chocolate. Theobromine has an antitussive effect superior to codeine by suppressing vagus nerve activity. Theophylline is a drug, a phosphodiesterase inhibitor, that is widely used in therapy for respiratory diseases. It is naturally found in black tea and green tea. The main actions of theophylline are relaxation of bronchial smooth muscle, positive inotropic (increases heart muscle contractility and efficiency) and positive chronotropic (increases heart rate) impact. It lowers blood pressure and has some anti-inflammatory effect. While caffeine, theobromine and theophylline are biologically active paraxanthine, interestingly, is inactive and therefore also non toxic.

Theobromine, theophylline and 1,7-dimethylxanthine (paraxanthine) are isomeric molecules. While the first two alkaloids are contained in natural fruits the last material represents an artificially made analogue. The molecules differ by the positions of the 2 methyl groups on the double ring. The figure shows theophylline as an example

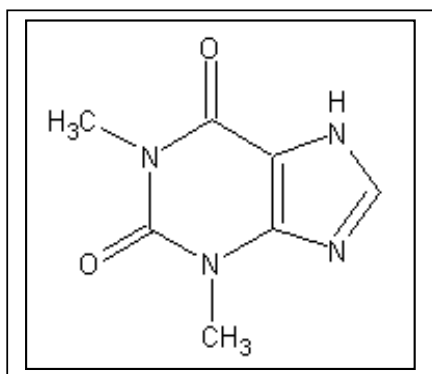


Fig. 1 Molecular structure of theophylline

In theobromine the methyl group between the two oxygens is moved to the upper nitrogen on the 5-ring. In 1,7-dimethylxanthine the bottom CH_3 is moved to this position. In caffeine with its third methyl group all three nitrogen sites on the double ring with single bonds bind a methyl group. This structure allows no isomeric form. The question is whether the similarity of molecular structure is found in a similarity of methyl dynamical behaviour. It is well known from the halomesitylenes and their derivatives that the hindering potential can strongly and often unexpectedly change with the methyl group position and neighborhood in the ring [1].

This experiment complements the investigation of lattice modes [2]. Two techniques were used to characterize the methyl rotational dynamics: the fixed window technique (FW) and real spectroscopy. The figures 2 shows a spectrum comparing theophylline with a tunneling band at about $16\mu\text{eV}$ and 1,7-dimethyl-xanthine without. Fig 3 reproduces the FW scan of theophylline. The intensity step at low temperature is a sign beginning stochastic reorientation. The corresponding soft rotational potential is consistent with the observed large tunnel splitting. The decay looks even to be a superposition of two dynamic processes. A similar two step behaviour is observed for theobromine. Caffeine and 1,7-dimethyl-xanthine show the corresponding decays at higher temperatures and as theobromine no tunnel transition. Further studies are planned.

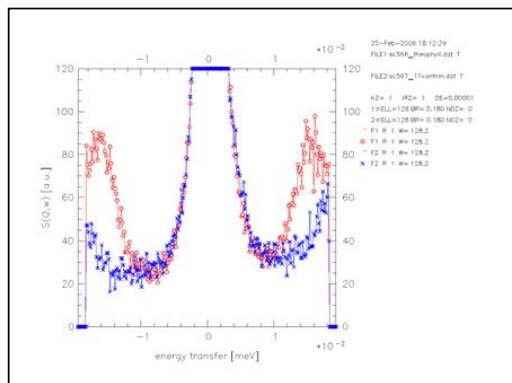


Fig. 2 spectra of theophylline (ooo) and 1,7-dimethyl-xanthine

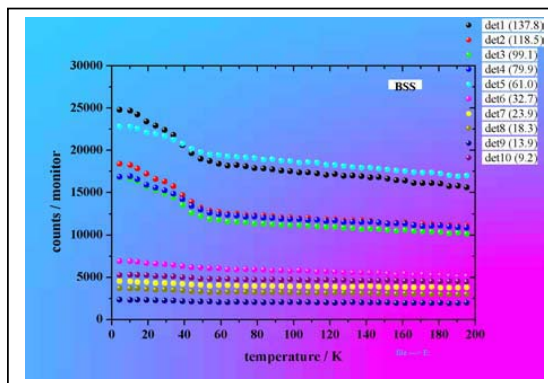


Fig. 3 Fixed-window scan of theophylline.

Despite of close structural similarities of the molecules there are clear differences in the spectra. The data analysis is in progress and will be based on DFT and lattice dynamical calculations.

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 [2] Experimental Reports FRJ2 2005, this volume, Report S29-05-006



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

Proposal number:	BSS-05-023		
Experiment title:	Hydrogen dynamics in doped and undoped sodium alanate		
Dates of experiment:	25.01.-29.01.2006 and 17.02.-26.02.2006	Date of report:	02.06.2006
Experimental team: Names	Addresses		
Shi, Qing Jacobsen, Hjalte S. Lefmann, Kim Vegge, Tejs	Materials Research Department Risø National Laboratory, Building 229 Frederiksborgvej 399, P.O. Box 49 DK-4000 Roskilde, Denmark		
Local Contact:	Michaela Zamponi		

Experimental report text body

Introduction

In 1997 Bogdanovic and Schwickardi [1] discovered that transition metal doped sodium alanate, NaAlH_4 , reversibly ab- and desorbs hydrogen at near ambient conditions. Since then the so-called complex hydrides have dominated the international research in solid-state hydrogen storage. The theoretical hydrogen storage capacity in complex hydrides is very high; upwards of 20 weight percent. However, little information is available about the catalytic effect of titanium on cyclic hydrogen ab- and desorption. Apart from the addition of Ti-based compounds, in particular TiCl_3 , the hydrogen kinetics can also be improved by decreasing grain size [2]. Although a number of experiments aimed at investigating the hydrogen dynamics in NaAlH_4 and Na_3AlH_6 have been performed [3], no conclusive knowledge about the possible catalytic effect on local hydrogen motion, rotation and long-range diffusion has been obtained at present. Quasielastic neutron scattering (QENS) was proposed for providing information of these types of processes.

Experimental

The QENS measurements of undoped NaAlH_4 and Na_3AlH_6 , and similar samples doped with 4 mol% TiCl_3 , were performed at the BSS instrument of FRJ-2, Jülich. All four sample powders were prepared by high energy ball milling which was used to disperse the catalyst and lower relaxation times. All materials handling was performed in an argon-filled glove box and a 0.1 mm Al sandwich sample container was employed to minimize multiple scattering. First, inelastic temperature scans in a large temperature range were performed to reveal the presence of temperature dependent structural and dynamic effects. The neutron backscattering measurements were performed continuously on the same geometry to obtain the quasielastic spectra.

Results

The results of the elastic temperature scan on Na_3AlH_6 are shown in Figure 1. No substantial temperature drops are observed at low temperatures, but a slow drop is observed at high temperatures.

Figure 2 shows the QENS spectra of undoped Na_3AlH_6 at different temperatures, where only the highest temperatures display a quasielastic broadening. Due to safety considerations we were unfortunately unable to go to higher temperatures

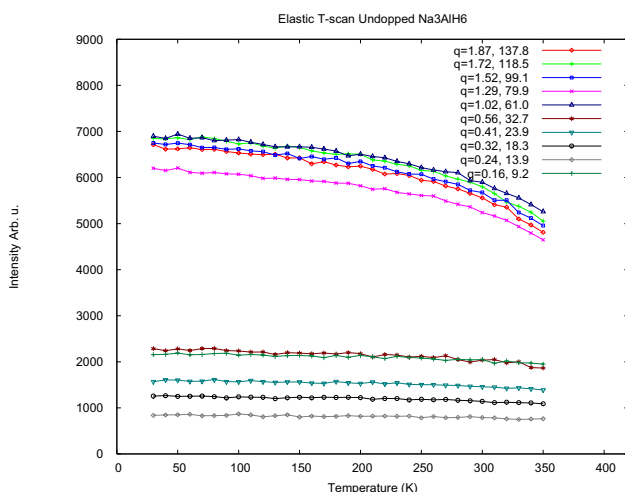


Figure 1

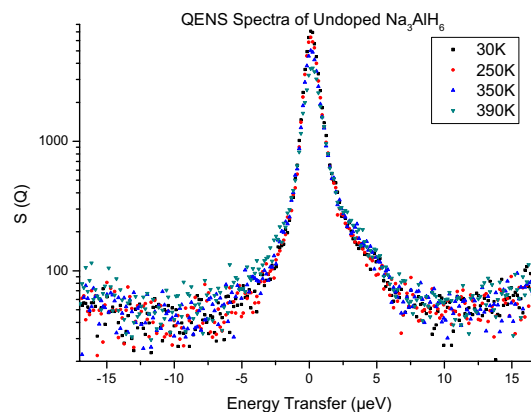


Figure 2

For each sample, QENS spectra were obtained at three-four different temperatures, and the data were processed by standard procedures. The instrumental resolution function was determined from the measured QENS spectra of each sample at low temperature (30K), and a quasielastic broadening of the signal was observed at temperature above 290K. The Lorentzian halfwidth of the quasielastic component is proportional to the hydrogen hopping rate and the diffusion constant. Using the Chudley-Elliot model [4] to describe the scattering vector dependence of the quasielastic Lorentzian halfwidth as a function of scattering vector can describe hydrogen jump diffusion in solids.

The long range hydrogen diffusion is found to be minimal, even when the materials are doped with TiCl_3 , and the primary effect of the dopants can therefore be concluded not to be increased hydrogen diffusion in sodium alanate. The analysis of the processed data is currently being finalized and compared to values from density functional theory (DFT) calculations [5].

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- [5] J. Voss, Q. Shi, H.S. Jacobsen and T. Vegge (to be published).



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

Proposal number:	BSS-05-024		
Experiment title:	Nature of Ag⁺ motion in silver iodide close to the superionic transition		
Dates of experiment:	Feb 6 th to Feb 12 th 2006	Date of report:	May 17 th 2006
Experimental team:			
León, Carlos	GFMC, Dpto. Fisica Aplicada III, Universidad Complutense Madrid Madrid 28040, SPAIN		
González, Miguel Angel ²	Instituto de Ciencia de Materiales de Aragón & Institut Laue-Langevin 6 rue Jules Horowitz B.P. 156, 38042 Grenoble Cedex 9 (France)		
Local Contact:	Michaela Zamponi		

Experimental report text body

Objectives:

It is well known that AgI undergoes a superionic transition at 420 K in which the ionic conductivity increases about four orders of magnitude. We have previously performed Admittance Spectroscopy measurements that show that this dramatic increase of ionic conductivity is preceded by a continuous and smooth change in the dynamics of silver ions. In order to confirm the validity of our interpretation of the ionic conductivity measurements using an independent technique we performed a neutron scattering experiment aimed to probe directly the dynamics of the silver ions.

Results:

Before starting with the inelastic scans, and in order to choose the appropriate temperatures for them, we performed several (30 minute long) elastic scans in the temperature range 300 - 420 K looking for any changes in intensity due to silver ion hopping. However, the elastic peak intensity was always rather low, and did not show any step or change in slope with increasing temperature. Then we decided to start with an inelastic scan at room temperature for 24 hours. The scattering signal observed was quite poor in all detectors, except in two of them due to bragg reflections at the corresponding Q ranges. When correcting for resolution and background, the signal was indistinguishable from noise. We tried then to see any difference at a higher temperature, 417 K, close to the superionic transition from the beta to the alpha phase. But again the signal was indistinguishable from noise.

Unfortunately, it seems that the energy range explored in a backscattering experiment does not allow to investigate silver ion hopping dynamics in the beta phase, even at the highest temperatures close to superionic transition. The smaller energies / longer time scales accessible by a neutron spin-echo experiment may be more appropriate for it. We can not discard, however, that the low intensity of the inelastic scattering signal was just a consequence of the high absorption in this material.



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

Proposal number:	BSS-05-026		
Experiment title:	Side-group motions of PMMA close and above the glass transition		
Dates of experiment:	09.01.-15.01.2006	Date of report:	22.06.2006
Experimental team: Names	Addresses		
Anne-Caroline Genix Arantxa Arbe Juan Colmenero Dieter Richter	Donostia International Physics Center, Apdo. 1072, 20080 San Sebastian, SPAIN Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ Dpto. de Física de Materiales, UPV/EHU, , “ , “ , “ IFF, FZJ, Jülich, Germany		
Local Contact:	Andreas Wischnewski		

Experimental report text body

The aim of this experiment was to investigate the side-group dynamics in syndiotactic poly(methyl methacrylate) (PMMA) ($T_g=400\text{K}$) through the hydrogen motions. The dynamics of the side group is believed to play an essential role in the β -relaxation of this polymer. Large amplitude motions involving 180° flips around the C-C bond connecting the main chain and the ester group have been found from NMR studies close to the glass transition [1]. Jumps of even larger amplitude have recently been observed by us for the ester-group hydrogens from fully atomistic MD-simulations [2].

The sample studied was PMMA-d5 with both the main chain and the α -methyl group deuterated (see inset in Fig.1). In this way, the scattering is dominated by the incoherent contribution of the hydrogens of the ester methyl group. The BSS measurements have been performed at 6 temperatures: 4K, each 25K between 425K and 500K, and 520K. The sample was placed in an Aluminum flat container at 45° with respect to the incident beam. The thickness was such that a transmission of ≈ 0.9 was calculated. With $\lambda=6.27\text{\AA}$ a Q-range of $0.16 \dots 1.87\text{\AA}^{-1}$ was accessed and an energy window of $\pm 17\mu\text{eV}$ was explored. Measuring times of about 20 hours were employed to achieve reasonable statistics, as can be appreciated in Fig. 1. Vanadium and empty cell measurements were also carried out to correct the spectra.

From our last results obtained by DNS measurements [3] at 300K on the same sample, we know that the measured spectra contain a coherent contribution which will be non-negligible close to the first maximum of the corresponding static structure factor ($Q_{\text{max}} \approx 0.8 \text{\AA}^{-1}$). The Q-dependence of the characteristic times for the collective motions can be determined from our MD-simulations on PMMA at 580K and 540K. In Refs [2, 3],

it has been shown, that the structural and dynamical properties of PMMA are well reproduced by our MD-simulations allowing a 65K temperature shift. Thus, for the quantitative analysis of the BSS spectra at 520K and 475K, we described the coherent contribution by the Fourier transform of a stretched exponential function, $\exp[-(t/\tau)^\beta]$, with τ and β fixed from the MD-results at 580K and 540K, respectively. As a first approach, the contribution related to the incoherent scattering in the sample was also described by the Fourier transform of a stretched exponential function with β fixed to 0.5. The global side group dynamics is described by the sum of both functions where the respective proportions to the total scattering are given by the DNS data [3]. As can be seen in Fig.1, this fitting procedure delivers a reasonable description of the experimental data and allows determining the characteristic timescales for incoherent scattering. The results are displayed in Fig. 2 where they are compared to i) the timescales issued from the MD-simulations for the self motions of the ester hydrogens and ii) the data previously obtained by us from BSS measurements on PMMA-d3 [4]. In the PMMA-d3 sample, only the ester methyl group was deuterated, which allowed accessing the dynamics of the main-chain and α -methyl group hydrogens [2, 4]. In Fig. 2, the characteristic times of self motions of the side groups in PMMA are significantly faster than those related to the main chain and α -methyl group, in good agreement with the MD-simulations results. However, the difference in the experimental timescales for main chain and ester side group seems to be more important in the high-Q range, whereas the MD-results suggest an increasing difference when moving towards lower-Q values. Further analysis is now needed to get deeper insight in the complex dynamics of the side groups in PMMA.

References:

- [1] K. Schmidt-Rohr et al, *Macromolecules* 27, 4733 (1994)
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- [3] A.-C. Genix, A. Arbe, F. Alvarez, J. Colmenero, W. Schweika, D. Richter, *Macromolecules* 39, 3947 (2006)
- [4] A.-C. Genix et al, Experimental Report BSS-05-006

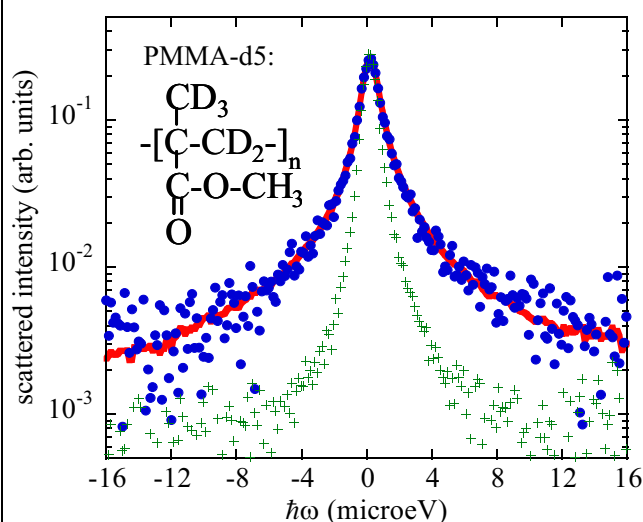


Fig. 1: Scattering function measured at $Q = 1.02 \text{ \AA}^{-1}$ for PMMA-d5 at 520K. The solid line is a fitting curve by means of the procedure described in the text to describe the overall dynamics of the side groups. The resolution function (PMMA-d3 at 4K) is shown by the crosses.

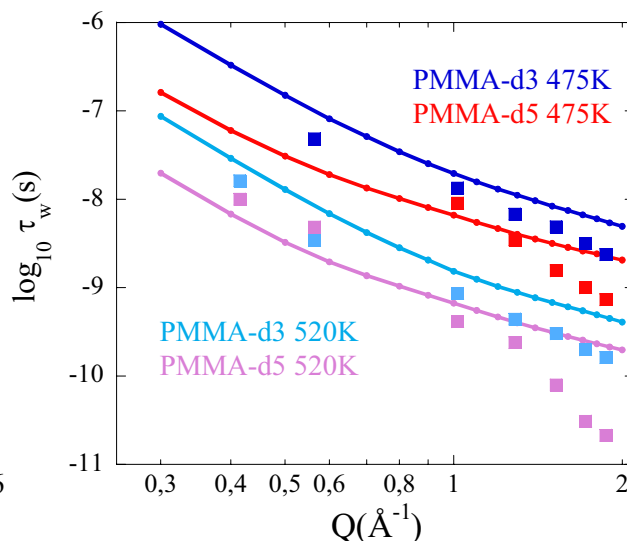


Fig. 2: Momentum transfer dependence in PMMA-d3 (blue) and PMMA-d5 (red) at 520K (light) and 475K (dark). Experimental results are represented by points and the corresponding MD-results by lines.



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

Proposal number:	BSS-05-027		
Experiment title:	Backbone dynamics in poly(ethyl methacrylate): a neutron scattering characterization of the process leading to randomization of the chain		
Dates of experiment:	16.01.-24.01.2006	Date of report:	22.06.2006
Experimental team: Names	Addresses		
Anne-Caroline Genix Arantxa Arbe Juan Colmenero Dieter Richter	Donostia International Physics Center, Apdo. 1072, 20080 San Sebastian, SPAIN Unidad de Física de Materiales, CSIC-UPV/EHU, “ , “ , “ Dpto. de Física de Materiales, UPV/EHU, , “ , “ , “ IFF, FZJ, Jülich, Germany		
Local Contact:	Andreas Wischnewski, Werner Schweika		

Experimental report text body

The aim of this experiment was to investigate the segmental relaxation in poly(ethyl methacrylate) (PEMA) ($T_g=338K$) through the hydrogen motions. The sample studied was PEMA with deuterated alkyl side group. In this way, the spectra revealed the dynamics of the main-chain and α -methyl group hydrogens (see scheme), while the side-group contributions (CD_2 - CD_3) were "hidden" for neutrons.

The BSS measurements have been performed at 9 temperatures: 4K, 250K, 285K, 325K, 400K, 425K, 454K, 487K and 520K. The sample was placed in an Aluminum flat container at 45° with respect to the incident beam. The thickness was such that a transmission of ≈ 0.9 was calculated. With $\lambda=6.27\text{\AA}$ a Q-range of $0.16 \dots 1.87\text{\AA}^{-1}$ was accessed and an energy window of $\pm 17\mu\text{eV}$ was explored. Measuring times of about 21 hours were employed to achieve reasonable statistics, as can be appreciated in Fig. 1. Vanadium and empty cell measurements were also carried out to correct the spectra. In addition, we performed DNS measurements on the same sample at 20K, 300K, 319K, 344K, 370K, 400K, 438K, 442K, by using the same container as for BSS. We used a wavelength of $3.3\text{\AA}$ and measuring times of one hour were employed. Measurements of NiCr, Vanadium and empty cell were also carried out to correct the experimental data. DNS results are crucial for the proper dynamic (BSS) data correction and analysis. Results obtained at 300K are presented in Fig. 2 where two clearly distinguishable peaks can be observed at about 0.6 and $1.3\text{\AA}^{-1}$, in good agreement with a recent WAXS study [1] on this sample.

From our last results obtained by BSS and MD-simulations on PMMA [2, 3], we expected that, also for PEMA, the quasielastic broadening of the BSS spectra below T_g would only relate to the α -methyl group rotation. The

quantitative analysis of the spectra at 250K, 285K and 325K in terms of methyl group rotation delivers a very good description of the experimental data when using the parameters previously obtained by us in PMMA for the α -methyl group rotation (see Fig. 1). As expected, the increase of the side chain length from PMMA to PEMA does not seem to affect such localized motion. Above 338K, additional broadening is observed that should be attributed to the segmental relaxation. In a first approach, we will assume statistically independent rotation of the α -methyl group and segmental relaxation. Then, the global dynamics can be described by the convolution of both functions. In this framework, the α -methyl group rotation can be taken into account by construction of an "effective resolution" including the quasielastic broadening expected from this motion properly weighed by the relative abundance of such atoms and the appropriated EISF [3]. The segmental dynamics contribution will be described by the Fourier transform of a stretched exponential function, $\exp[-(t/\tau)^\beta]$.

The strongly heterogeneous and anisotropic motions proposed from recent NMR studies [4] should give rise to severe deviations from Gaussian behavior of the H-segmental dynamics. Therefore, the determination of the Q-dependence of the timescales characteristic for segmental motions is crucial to check the NMR results on this polymer.

References:

- [1] M. Wind et al., J. Chem. Phys. **112**, 014906 (2005),
- [2] A.-C. Genix, A. Arbe, F. Alvarez, J. Colmenero, L. Willner, D. Richter, PRE **72**, 31808 (2005)
- [3] A.-C. Genix, A. Arbe, F. Alvarez, J. Colmenero, B. Farago, A. Wischnewski, D. Richter, submitted to Macromolecules
- [4] M. Wind et al., PRL **91**, 155702 (2003); M. Wind et al., Macromol. Chem. Phys. **206**, 142 (2005).

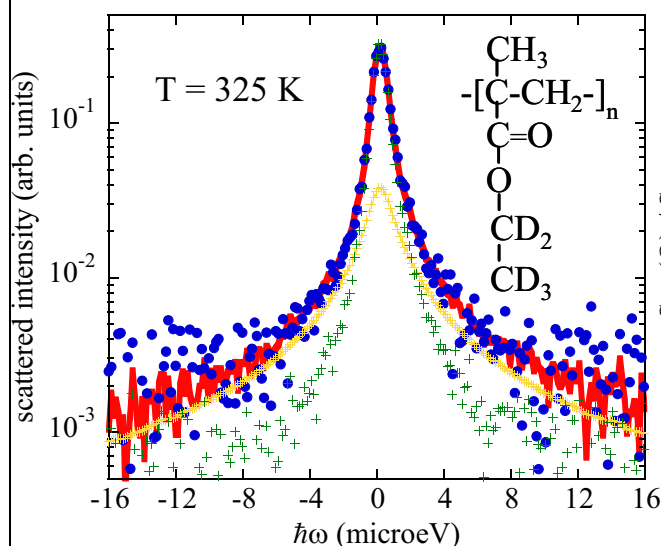


Fig. 1: Scattering function measured at $Q=1.9\text{\AA}^{-1}$ and 325 K for PEMA with deuterated alkyl groups. The red solid line is a fit by means of methyl group rotation. The yellow line shows the quasielastic component corresponding to methyl-group dynamics. The resolution function is shown by the crosses.

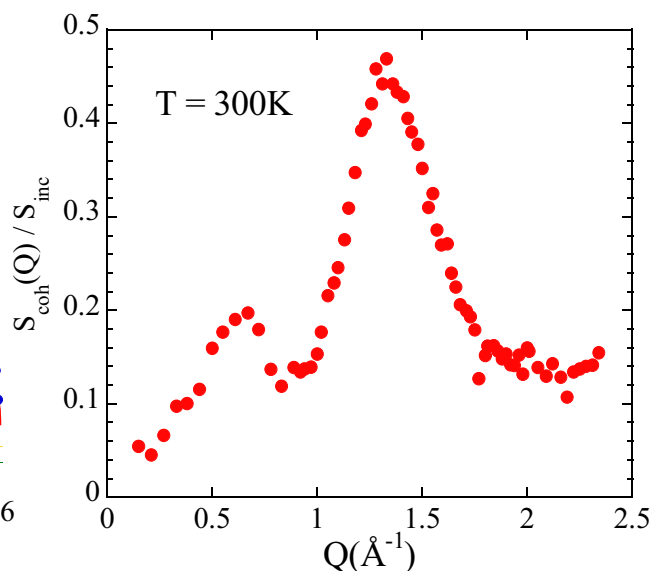


Fig. 2: Ratio between the coherent and incoherent scattering intensities measured by means of DNS at 300K in PEMA with the alkyl side group deuterated.



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

Proposal number:	BSS-05-028		
Experiment title:	Rotational dynamics of methyl groups in the chloranilic acid plus 2,6-dimethylpyrazine complex		
Dates of experiment:	2.9.2005, 6 days	Date of report:	25.2.2006
Experimental team:			
Names	Addresses		
A. Pawlukoje M. Prager	Institute of Nuclear Chemistry and Technology, Warsaw, Poland Forschungszentrum Jülich		
Local Contact:	H. Grimm		

Experimental report text body

The study of charge transfer/H-bond complexes using methyl rotational potentials as sensitive local probes is extended from the first investigated complex tetramethylpyrazin:chloranilic acid (TMP:CLA) [1] towards new systems. The actual compound, 2,6-dimethylpyrazin(DMP):CLA, was chosen since on the one hand the pure 2,6-DMP is already carefully studied with respect to structure [2] and dynamics [3] and since on the other hand the crystal structure of the complex is also known [4]. In pure 2,6-DMP the methyl groups feel a weak potential resulting in large tunnel splittings [3]. Therefore the influence of an electron acceptor neighbour on the lattice dynamics and methyl rotation in the molecular alloys of the charge-transfer type is expected to be accessible to spectroscopy.

The backscattering spectrometer was used in its centered configuration. A tunnel transition in the protonated DMP:CLA complex was observed at $3.30\mu\text{eV}$ (fig. 1, 000). It shows an intensity of about 6.4% of the elastic intensity. If one calculates this ratio for the mean momentum transfer $Q=1.6\text{\AA}^{-1}$ theoretically for the case of one resolved and one unresolved (=elastic) tunnel band at the presence of the 2 protons of the chloranilic acid one gets a value 8.3%. Keeping in mind that there are other sources of elastic scattering this is a good confirmation that the crystal structure determined at $T=100\text{K}$ is unchanged down to the $T=4.5\text{K}$, the sample temperature in the present experiment.

The tunneling transition was investigated as a function of temperature. The line is too near to the elastic line to allow the more interesting line broadening to be reliably quantified. The temperature evolution of the position could be evaluated, however, and is shown in an Arrhenius presentation in fig. 2. The solid line represents a fit and gives an activation energy $E_S=16\text{meV}$ what is not too different from the observed energy of the methyl librational mode.

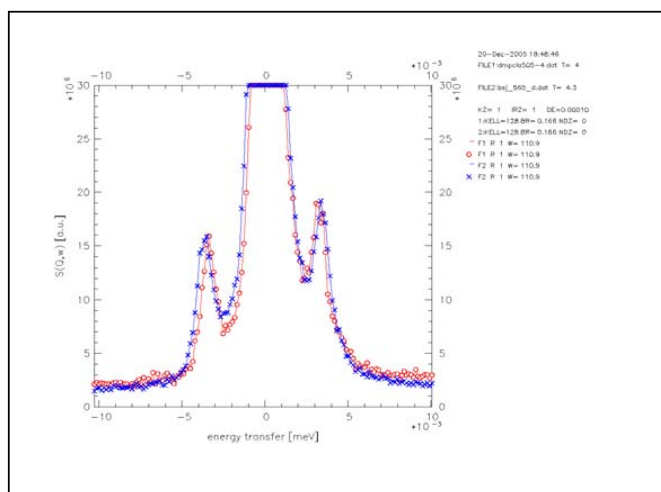


Fig. 1: Spectra of 2,6-DMP:h-CLA (ooo) and 2,6-DMP:d-CLA (xxx). Sample temperature $T=4.5\text{K}$.

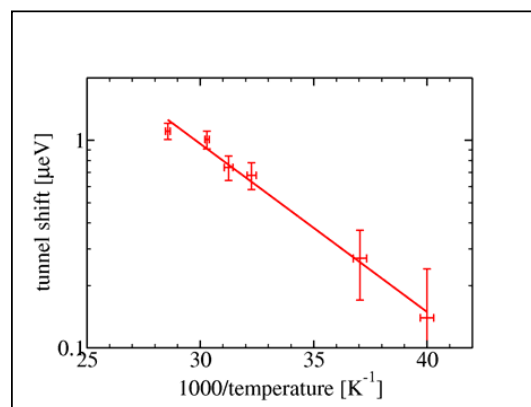


Fig. 2: Shift of the tunnel peak of 2,6-DMP:h-CLA with temperature. Arrhenius-plot.

Finally, the influence of deuteration of the cloranilic acid, i.e. the hydrogen bond, is searched for. Fig. 1, xxx, shows the spectrum of 2,6-DMP:d-CLA. The tunnelling band is unexpectedly found at weakly higher energy than in the protonated material. Usually the opposite effect is observed: the better localisation of deuterons causes a hardening of the material.

The methyl rotational potential in the 2,6-DMP:CLA complex is stronger as in pure 2,6-DMP. This means that intermolecular interaction strongly contributes to the rotational potential. The dominance of steric effect is supported by the opposite change of the hindering barrier observed in TMP:CLA [1]. An effect of charge transfer from the donor to the acceptor species of a complex is expected to cause changes of similar sign. Our data show that - if such an effect exists - it is largely hidden by the overwhelming dominance of structural changes.

A final data evaluation is in progress.

- [1] M Prager, A Pawlukojs, L Sobczyk, E Grech, H Grimm, J. Phys.: Condens. Matter 17,5725(2005)
- [2] E. KaiserMorris, A. Cousson, W. Paulus, F. Fillaux, Acta Cryst. E57,o1116(200)
- [3] B. Nicolai, E. Kaiser, F. Fillaux, G.J. Kearley, A. Cousson, W. Paulus, Chem. Phys. 226,1(1998);
- [4] W Sawka-Dobrowolska, G Bator, L Sobczyk, E Grech, J Nowicka-Scheibe, A Pawlukojs, Struct. Chem., in press;



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

Proposal number:	BSS-05-029		
Experiment title:	Supplementary backscattering experiments on a glass-forming microemulsion		
Dates of experiment:	28.11.–06.12.2005	Date of report:	06.06.2006
Experimental team: Names	Addresses		
Mayorova Maria Zorn Reiner	Institut für Festkörperforschung, Forschungszentrum Jülich Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	Michaela Zamponi		

Experimental report text body

The increasing demand of materials which are required to perform on spatial scales as small as several nanometers challenges our understanding of how geometrical confinement and interfacial situations change the properties of condensed matter. In the present work dynamics of viscous PG near its glass transition is to be explored for the case of soft confinement. Soft confinement is realized by a microemulsion as described below. For this purpose a three component system using PG as polar phase, decalin as nonpolar phase, and ionic surfactant AOT was chosen. The glass transition temperatures of the bulk PG and decalin are $T_g=167$ K and $T_g=135$ K, respectively. This microemulsion with reverse micelles is stable and optically clear. The sample has the composition (by weight of undeuterated compounds): PG 10,2%, AOT 36,1%, Decalin 53,7%.

To get information about slow dynamics, incoherent inelastic spectra have been obtained with back scattering spectrometer PI and then after Fourier transformation have been combined with time-of-flight data from NEAT (HMI, Berlin). To extract information concerning confined PG, data obtained for the completely deuterated microemulsion were subtracted from data for microemulsion with protonated PG and deuterated other components. Measurements were performed for two temperatures (230K and 270K). Unfortunately, the sample crystallized at 230 K so that the spectra taken at that temperature could not be evaluated. This happened completely unexpected because the temperature was reached by cooling the sample and in previous experiments (e.g. BSS-05-009) this was sufficient to avoid crystallization.

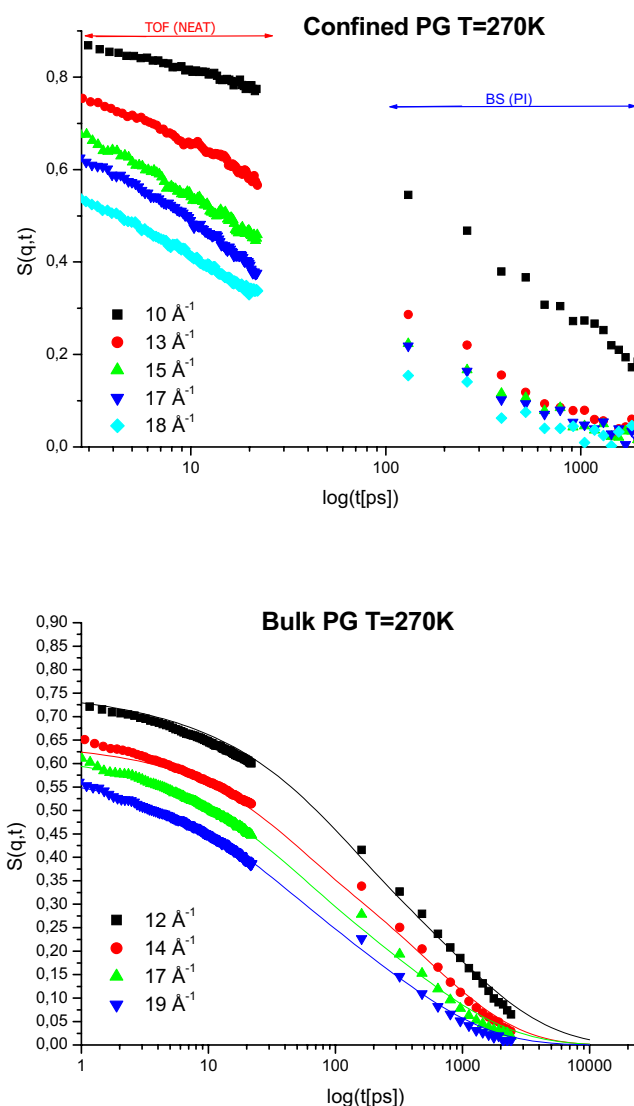


Fig. 1 Comparison of the intermediate scattering function $S(Q,t)$ of PG confined in the microemulsion with bulk PG.

The comparison of the scattering function behavior for bulk and confined PG (Fig.1) provides information that in the case of confined PG the α relaxation is more stretched. This is a quite common behavior for this type of relaxation in confined glass forming liquids as the α relaxation is related to the cooperative group motion. The interaction between interfacial liquid layer and the static wall (hard confinement) or fluid environment (soft confinement) leads to existence of molecular groups with dynamics affected by the host material, which in turn results in stretching of α relaxation.



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

Proposal number:	BSS-05-030		
Experiment title:	Temperature dependence of hemoglobin dynamics in intact erythrocytes: A neutron scattering study		
Dates of experiment:	16.-17.02.2006	Date of report:	05.06.2006
Experimental team: Names	Addresses		
A. Stadler J. Zaccai G. Artmann	ILL, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, France ILL, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, France FH Aachen, Ginsterweg 1, 52428 Jülich, Germany		
Local Contact:	Michaela Zamponi		

Experimental report text body

Incoherent elastic neutron scattering of red blood cells (RBC) has been measured with the spectrometer BSS. The glycocalix matrix of RBC has been removed by neuramidase treatment, intracellular hemoglobin has been stabilized by decarboxylation with CO. A rather dilute concentration of RBC in H₂O has been measured to prevent the cells from destruction and to ensure the possibility of comparison with existing micropipette aspiration data [1], as a consequence only rather low intensity was measured at high q^2 -values.

A diffusion model [2] could be fitted to the measured intensity according to

$$S(q^2) = \frac{C}{1 + \frac{D}{\Gamma} \cdot q^2}, \quad (1)$$

the diffusion coefficient is named by D, Γ has got the value of $7.6 \cdot 10^{-8} \text{ cm}^2/\text{s}$ in the case of BSS and the coefficient C was introduced to take into account the temperature dependent loss of intensity.

The fit of equ. (1) is shown in Fig. 1 for the minimal and maximal measured temperatures. The coefficient C was determined by extrapolating $S(q^2)$ to $0 \text{ \AA}^{-2}$, the temperature behaviour of C is shown in Fig. 2. The breakpoint at around 312K can be interpreted with the onset of large-range motions which are out of the time-space window of the instrument BSS.

The determined diffusion coefficient increases rather linearly with temperature and is shown in Fig. 3.

A more detailed data analysis is in the way. Additional neutron scattering experiments to study the thermal motions of intracellular hemoglobin of RBC are in preparation.

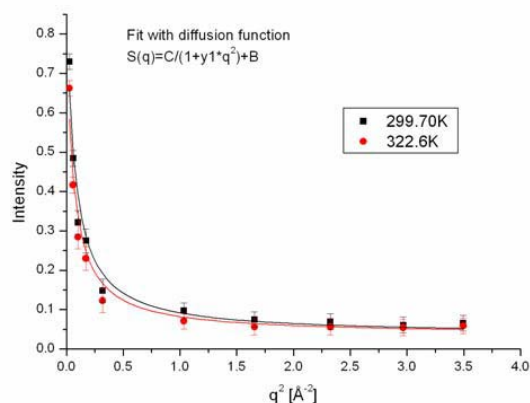


Fig. 1 Fit of model of free diffusion to the measured intensity $S(q^2)$ at two different temperatures.

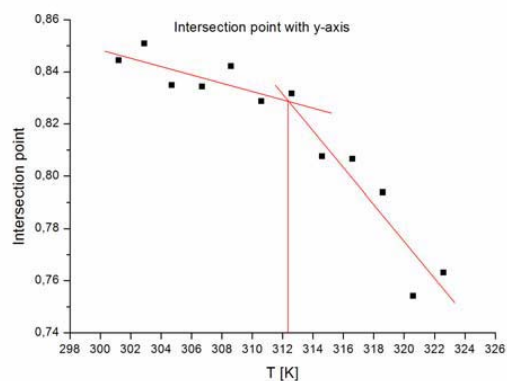


Fig. 2 At $T \approx 312K$ the sharp drop of $S(q^2 \rightarrow 0 \text{ Å}^{-2})$ indicates the onset of long-range motions which are out of the time-space window of the neutron spectrometer.

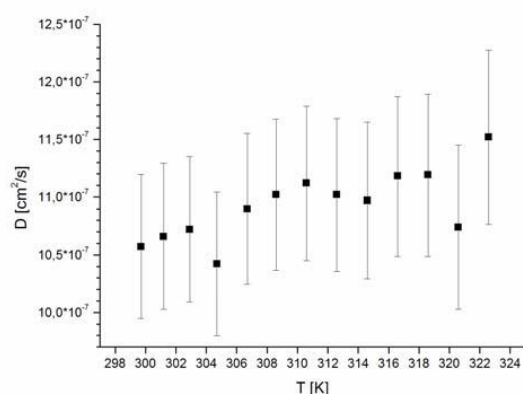


Fig. 3 The determined diffusion coefficient increases with temperature.

[1] Artmann G.M., Kelemen C., Porst D., Büldt G., Chien S. (1998) Temperature transitions of protein properties in human red blood cells. *Biophys. J.*, 75: 3179-3183

[2] Gabel F. (2005) Protein dynamics in solution and powder measured by incoherent elastic neutron scattering: the influence of Q-range and energy resolution. *Eur. Biophys. J.*, 34:1-12



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

Proposal number:	BSS-06-001		
Experiment title:	Dynamics of syndiotactic polypropylene		
Dates of experiment:	12.02.-14 .02.2006	Date of report:	23.05.2006
Experimental team: Names	Addresses		
M.Zamponi A.Wischnewski	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	M. Zamponi		

Experimental report text body

The topological confinement in polymer melts can be explored by mechanical (rheology) and microscopic (neutron spin echo (NSE) spectroscopy) experiments. For the so far investigated polymers (polyethylene (PE), polyethylpropylene (PEP)) the value for the confinement length obtained by NSE is considerable higher than the rheological value, however the ratio is about the same. To clarify if the observed discrepancies stem only from the different experimental techniques or from two different length scales in the polymer melt, the dynamical behaviour of a polymer with different properties shall be explored. If the deviations are only an experimental 'artefact' they should be comparable for all the polymers, independent on the properties. On the other hand if the two methods explore two different length scales (longitudinal and transversal confinement length) the ratio for a very stiff polymer should be different than for PE and PEP. Syndiotactic polypropylene (s-PP) is an ideal candidate since the stiffness parameter (C_{∞}) is significantly larger than for the other polymers but at the same time the segmental friction is expected to be low.

As a preparatory study for a proposed neutron spin echo experiment, neutron back scattering on a fully protonated s-PP sample has been performed. Inelastic scans at two temperatures (463K and 483K) have been done (fig.1). The obtained spectra show a clear quasi-elastic broadening, the observed temperature dependence is only weak. The quasi-elastic broadening can be described by a stretched exponential function with $\beta=0.5$ (Rouse expectation). The characteristic relaxation time is then $\tau=9\pi/(Wl^4)*q^{-4}$, where the Rouse rate $W=3kT/\xi l^2$ is determined by the segmental friction ξ . For each q-value the relaxation time has been fitted. Then from the resulting q-dependence of the time scale the Rouse parameter Wl^4 can be estimated (fig.2). From the fit Wl^4 has been calculated to be about $20000\text{\AA}^4\text{ns}^{-1}$ at a temperature of 483K ($13500\text{\AA}^4\text{ns}^{-1}$ at 463K). Using this value in the reptation model the dynamic structure factor can be calculated, showing that the segmental motion is in the right time and q-range to be observed with the high resolution of NSE.

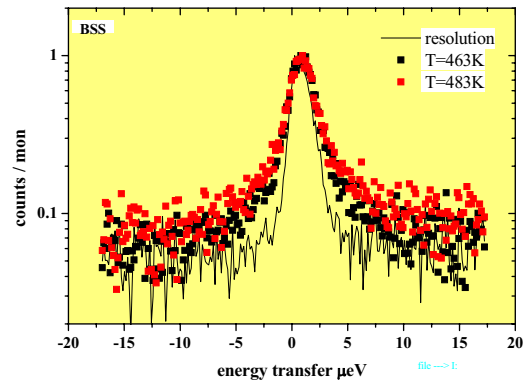


Fig.1: Neutron backscattering spectra of s-PP at two different temperatures in comparison to the resolution (line) for $q=0.24\text{\AA}^{-1}$.

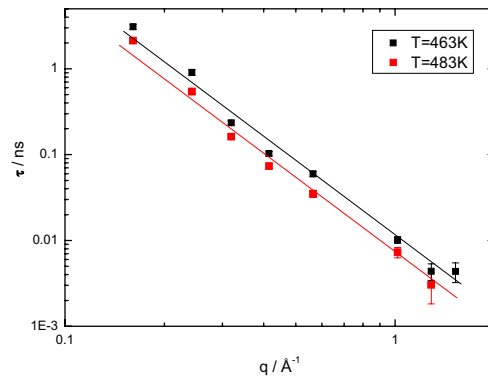


Fig.2: Characteristic relaxation time in dependence of q obtained from the BSS spectra. Lines: expected q -dependence $\tau = a \cdot q^{-4}$.



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

Proposal number:	BSS-06-002, BSS-06-003		
Experiment title:	Dynamics of intercalated PEO in an PEO-MMT-nanocomposite		
Dates of experiment:	15.3.2006 - 21.3.2006 21.4.2006 - 1.5.2006	Date of report:	9.5.2006
Experimental team: Names	Addresses		
Tobias Zacherle	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Andreas Wischnewski	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Andreas Wischnewski Dr. Michaela Zamponi		

Experimental report text body

In these experiments we investigated the dynamics of PEO (Poly-ethylene-oxide) intercalated between silicate sheets in the PEO-MMT-nanocomposite. In recent years research in the field of nanocomposites has increased dramatically, focussing both on the favourable properties of these materials [1] and the fact, that they represent model-systems for 2-d confinement for polymers [2]. One is interested in possible differences that may occur in comparison to the behaviour of bulk-polymer.

As the sample-preparation is somewhat difficult, we compared in previous SANS-measurements different preparation methods, in particular:

1. The method of freeze-drying. In this procedure one dries the MMT-PEO-solution by freezing it first and then sublimating the solvent. One obtains a fluffy material which needs to be pressed afterwards and dried in the vacuum.
2. The method of distillation under low pressure (film-method). Here the solution is dried by slowly reducing the pressure and vapourising the solvent. A gelous kind of material is obtained, depending on the time of distillation and this gel is further dried in the air on the sample-container and then in the vacuum.

As the film-method proved to be the better choice, we decided to stick to this procedure for our BSS-samples. Nevertheless we prepared two different kinds of samples for the two BSS-experiments. For the first one, we used water (H_2O) as a solvent, for the second one heavy water (D_2O). The second samples were believed to yield better results due to the lower incoherent scattering of deuterated water.

In both cases significant broadening of the peaks could be observed, i.e. the dynamics is within the energy window of the spectrometer. In addition the curves show the expected behaviour that the peaks broaden with increasing temperature. In the first plot, the results for the samples prepared with water are shown:

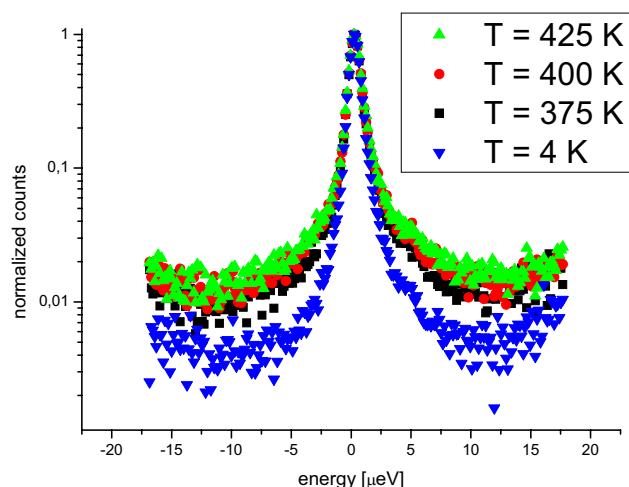
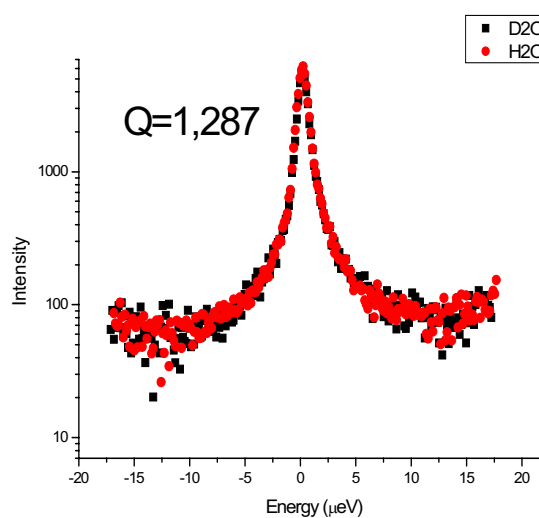
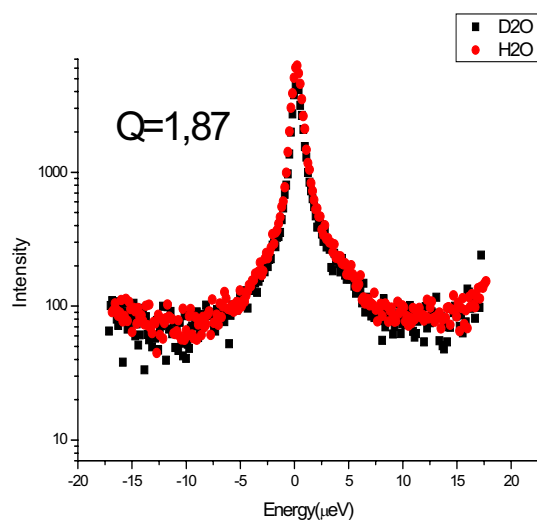


Fig1:
One sees clearly the broadening of the peaks with higher temperature. The slowest dynamics is obtained for the 4K resolution-curve, the fastest dynamics for the 425K measurement.

We were able to extract the corresponding relaxation-times τ , but a detailed analysis of the data is still ongoing.

In the second experiment – as already mentioned – we measured a sample for which D_2O was used as a solvent in the preparation-process. We did expect to see a rather big difference in the peaks, but it turned out that the two samples did behave very similar. Thus it can be concluded that the use of water or heavy water doesn't play a major role during the preparation for the drying in the vacuum seems to be very efficient in both cases. So there isn't any significant quantity of the solvent left in the sample.



On the two plots above, we show the results for the two experiments for two different Q-values. One sees, that the peaks are the same.

[1] S.S. Ray, M. Okamoto; Polymer/layered silicate nanocomposites: a review from preparation to processing; *Prog. Polym. Sci.* **2003**, 28, 1539-1641

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



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

Proposal number:	BSS-06-004		
Experiment title:	Multiple scattering of PEO/PMMA		
Dates of experiment:	08.04.2006 – 17.04.2006	Date of report:	22.05.2006
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Experimental report text body

It is well known for blend systems that the behaviour of each component is influenced by the presence of the second one. However, up to now, it is impossible to predict the properties of a blend based on what is known about the behaviour of the pure components [1].

In particular interesting are blends of components with very different glass transition temperatures T_g , i.e. the dynamics of the pure components is well separated in time.

A good candidate for a systematic study of this topic by neutron scattering is the miscible PEO / PMMA blend, a system with widely separated glass transitions ($T_g^{\text{PEO}} \approx 210 \text{ K}$, $T_g^{\text{PMMA}} \approx 400 \text{ K}$).

Our first investigations on this system (35% h-PEO / 65 % d-PMMA and 50 % h-PEO / 50 % d-PMMA) shows that the PEO component is very mobile, but the dynamics seems to be restricted to small length scales. Moreover, we found that the low Q data ($Q < 1 \text{ Å}^{-1}$) strongly deviate from the Debye-Waller-Factor (DWF), Eq. (1), which we found for the high Q data, see Fig. [1].

$$I = DWF = \exp\left(-\frac{Q^2 \langle u^2 \rangle}{3}\right) \quad (1)$$

Here, $\langle u^2 \rangle$ is the mean square displacement determined by the fast processes.

An explanation for this deviation may multiple scattering. Therefore, to estimate the multiple scattering effect, we measured the 35% h-PEO / 65% d-PMMA blend system with a different thickness of the samples: $d = 0.3\text{mm}$, 0.5mm and 3mm . The measurements were done at three temperatures $T = 375 \text{ K}$, 400 K and 425 K . For the proper data correction we determined the resolution of the instrument by measuring all samples at $T = 4 \text{ K}$ and the background by measuring the empty cell.

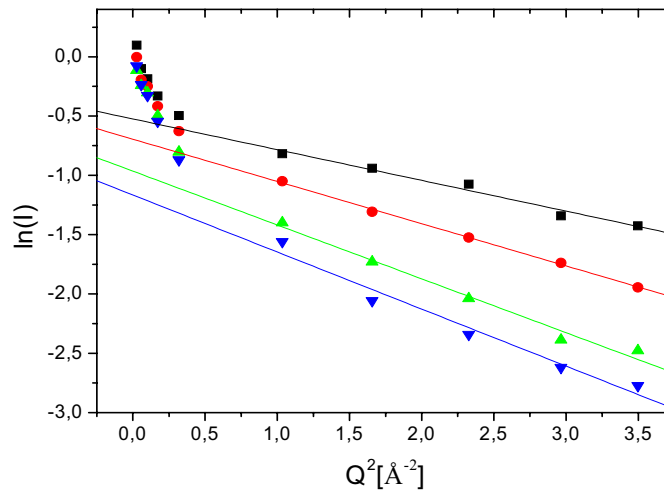


Fig. 1 Scattering intensity as a function of Q for the blend sample 35% h-PEO / 65% d-PMMA of 1mm thickness at different temperatures (black squares – 350 K, red circles – 375 K, green triangles up – 400 K, blue triangles down – 425 K). Solid lines represent fits with the DWF.

To have a good comparison of the scattering intensity we applied the identical fitting procedure to all data sets. The distribution function of relaxation times for the fast component PEO was fitted with the Kohlrausch-Williams-Watts (KWW) function. For the slow component PMMA we assume that it is stiff at the measured temperatures, so it contributes only to the elastic scattering. Thus the only fitted parameters were the total intensity I and the relaxation time τ of PEO, see Eq. [2]

$$I(Q, \omega) = DWF * FT \left\{ \left[f * \exp(-(t/\tau)^{0.5}) + (1-f) \right] * resolution \right\} \quad (2)$$

Here, f is the relative amount of quasielastic scattering coming from PEO in the blend system, this value is known from an earlier DNS measurement.

Comparing the results obtained for the total intensity (Fig. [2], data for the sample with $d=1\text{mm}$ coming from a previous BSS measurement, BSS-05-008), we observe that with increasing thickness of the sample up to 1mm, the scattering intensity decreases. Moreover, the deviation from the DWF for small Q seems to be systematic and is observed even for 0.3 mm thick sample. Clear evidence of multiple scattering is visible only for the 3 mm thick sample.

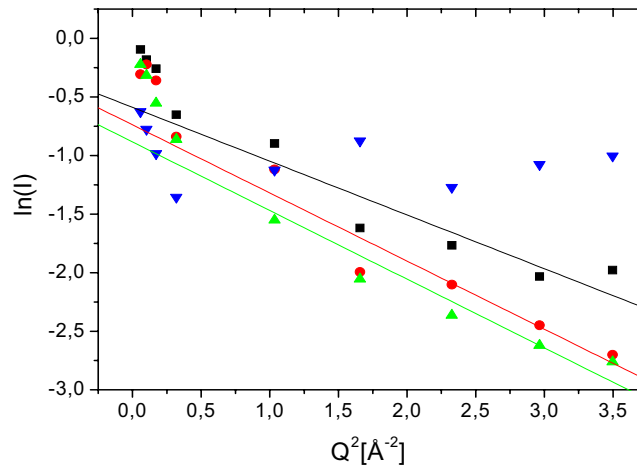


Fig.2 Scattering intensity of the blend sample 35% h-PEO / 65% d-PMMA as a function of Q at $T=425\text{ K}$ for different samples thickness (black squares – 0.3mm, red circles – 0.5mm, green triangles up – 1mm, blue triangles down – 3mm). Solid lines represent fits with the DWF.

[1] S. Hoffman et al., Physical Review Letters 85, 772 (2000)