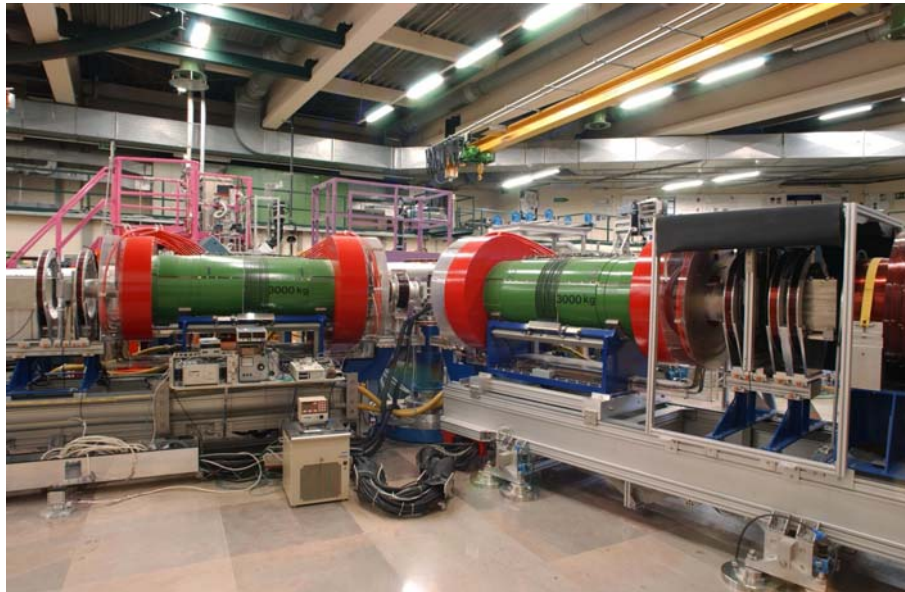


Neutron Spin Echo Spectrometer (NSE)



Instrument Parameters

Beam tube:	NLIIB curved guide
Monochromators:	polarizing multilayer mirror (FeGe) velocity selector (DORNIER) $\Delta\lambda/\lambda = 0.1$ (or 0.2)
Incoming beam - Cross section of guide: - Sample size:	4.5 cm (height) $\times$ 3 cm (width) 4 cm $\times$ 4 cm (max.)
Collimation:	by source and sample size or wire collimators $0.5^\circ \times 0.5^\circ$
Polarised neutron flux at sample ($\lambda = 8 \text{ \AA}$):	$8 \times 10^5 \text{ n/cm}^2 \text{ s}$ (natural collimation)
Wavelength range:	$\lambda = (8 \pm 2) \text{ \AA}$, alternative mirror $(6 \pm 2) \text{ \AA}$
Momentum transfer range:	$0.01 \dots 1.5 \text{ \AA}^{-1}$
Fourier time range (in STD set-up):	$0.04 \dots 48 \text{ ns}$
Max. field integral:	0.5 Tm
Analyzer:	$30 \times 30 \text{ cm}^2$ CoTi supermirror Venetian blind
Detector:	$32 \times 32 \text{ cm}^2$ cells ^3He multidetector

Instrument Responsible

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 Dr. Ralf Biehl Tel. +49-(0)-2461-61-4685 Email: ra.biehl@fz-juelich.de



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

Proposal number:	NSE-04-004		
Experiment title:	Study of the charged groups dynamics in polystyrene based random ionomers		
Dates of experiment:	03.02. – 04.02.2005 13.05. – 17.05.2005 01.10. – 04.10.2005	Date of report:	18 th May 2006
Experimental team: Names	Addresses		
Edoardo De Luca (Thomas Waigh – analysis)	Department of Chemistry, University of Durham, Durham, DH1 3LE, UK. (Biological Physics, Department of Physics and Astronomy, University of Manchester, Manchester, M60 1QD, UK.)		
Local Contact:	Ralf Biehl, Michael Monkenbusch		

Experimental report text body

The dynamics of phase separated micellar solutions of randomly sulphonated polystyrene ionomers in deuterated toluene were examined with neutron spin echo spectroscopy (NSE). The correlation functions demonstrated single exponential decays with a constant background offset. The relaxation rate (Γ) of the ionomer micelles in the q range 0.0268 to 0.131 Å⁻¹ were diffusive ($\Gamma \sim q^{-2}$) at small length scales with a hydrodynamic mesh size independent of molecular weight as expected for the collective diffusive mode of a cross-linked gel. At large length scales the scattering due to the phase separated network of micelles was stationary on time scales <20ns (**figure 1**). The results are in agreement with the model developed in previous small-angle neutron scattering experiments for concentrated solution of ionmeric micelles (**figure 2**) [1]. The NSE results for the associating ionomers are markedly different to the Zimm dynamics ($\Gamma \sim q^{-3}$) previously observed with semi-dilute and cross-linked polymers in a good solvent [2]. The ionomeric cross-links thus have a large impact on the chains dynamics at the nano second time scale. Increasing the temperature (T) of the samples causes the motion of the ionomer gel to increase in proportion to T/η (η is the viscosity, **figure 3**). No clear signature of the activated dynamics of the ionomeric stickers as a function of temperature was discernable.

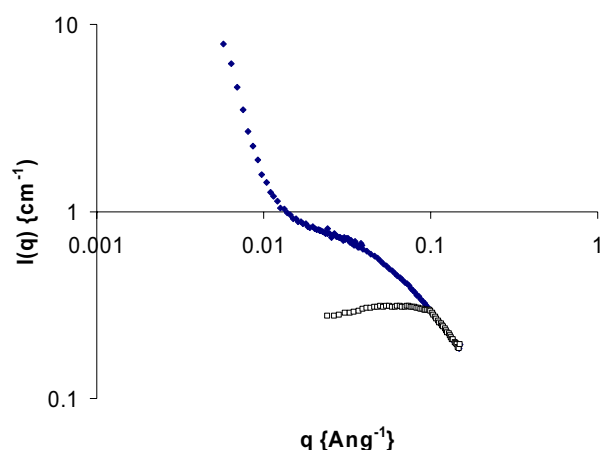


Figure 1. Small angle neutron scattering from 10%w/w random PSS ionomers (diamonds). The squares show the ergodic amplitude in the time window <20ns from NSE. These amplitudes are attributed to the motion of the internal gel dynamics of the ionomer micelles (**figure 2**).

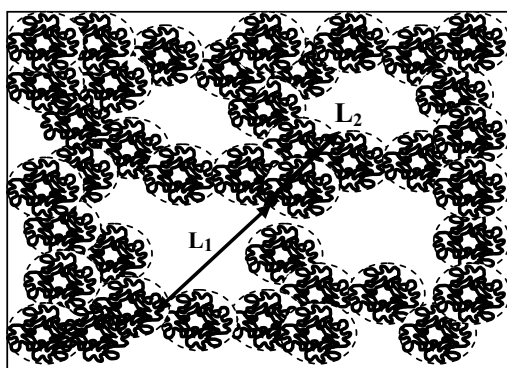


Figure 2. Morphology of random ionomer gels deduced from small angle neutron scattering. Two lengths scales are important; the average chord length (related to L_1 and L_2) of the microphase separated micellar structure and the average intrachain mesh size (ξ).

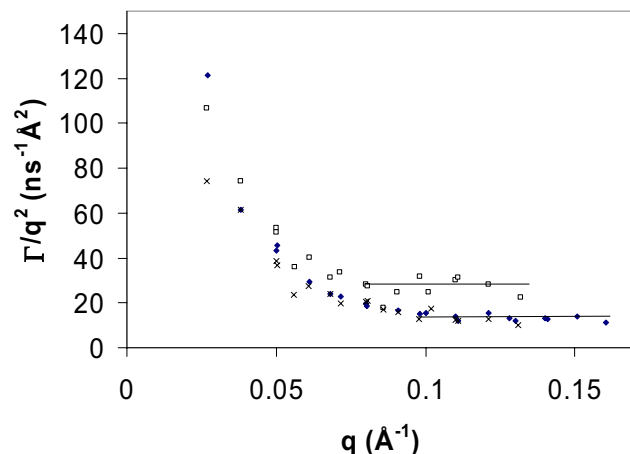


Figure 3. Relaxation rates for random PSS ionomers. Two different molecular weights (crosses and diamonds) are shown and samples at elevated temperatures (squares). The straight lines indicate the diffusive modes found at small length scales.

References

- [1] E. de Luca, T.A.Waigh, J.S.Kim, W.Hintzen, 'Phase separation in randomly charged polystyrene sulphonate ionomers', *Polymer*, 46, 2005, 7109-7117.
- [2] B.Ewen, D.Richter, B.Lehnen, 'Segmental diffusion of polymer molecules in solution as studied by means of quasi-elastic neutron scattering', *Macromolecules*, 12, 1980, 876-880.



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

Proposal number:	NSE-04-007		
Experiment title:	Local dynamics and entanglements of hydrogen-bonded polymers		
Dates of experiment:	04.03. – 11.03.2005	Date of report:	05.06.2006
Experimental team: Names	Addresses		
Adrian S. Muresan Wim H. de Jeu	FOM-Institute for Atomic and Molecular Physics Kruislaan 407 1098 SJ Amsterdam Netherlands		
Local Contact:	Dr. Michael Monkenbusch		

Experimental report

In this project we studied the segmental dynamics of equilibrium polymers formed by strongly directional quadruple hydrogen-bonded dimmers. We observed a clear effect of friction heterogeneity along the backbone of the self-assembled chains. The friction heterogeneity has been attributed to the hydrogen-bonding connector groups, which in our case are quite bulky in comparison to the hydrocarbon spacers that link pairs of them in the basic molecular building blocks.

The system studied consisted of units of 30-60 covalently bonded THF monomers with quadruple hydrogen-bonding ureidopyrimidinone (UPy) groups attached at each end (see Figure 1). Two different types of labelling A and B were prepared, illustrated in Figure 2. In labelling A the elementary chains (≈ 74 monomers) were identical and had 15% hydrogenated monomers distributed at random in a matrix of deuterated monomers. In labelling B we had a mixture of 15% hydrogenated elementary chains with ≈ 30 monomers and 85% deuterated elementary chains with ≈ 86 monomers. Due to the breaking and recombination of hydrogen bonds, the spatial distribution of the hydrogenated elementary chains was random. The two types of labelling A and B are qualitatively similar, the only difference being the size of the randomly placed hydrogenated unit: a single monomer in case A, a full elementary chain of ≈ 30 monomers in case B.

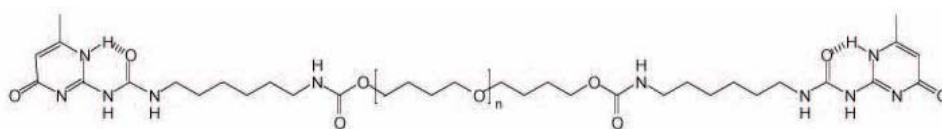


Figure 1. Chemical structure of the hydrogen-bonded polymer used. The two Upy groups at the ends of the single elementary chain pictured form four hydrogen bonds, giving rise to larger hydrogen-bonded polymers.

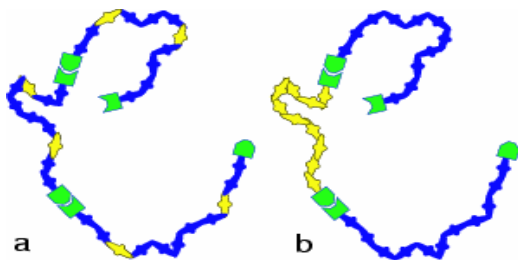


Figure 2. Schematic representation of the labeled polymeric systems A (a) and B (b). The deuterated blue and hydrogenated yellow monomers are covalently bonded while the green blocks represent the quadruple hydrogen bonding UPy groups.

The correlation functions for samples A and B as obtained by NSE at $T = 353$ K can at each q be well fitted by a function of the form $S(q, t) \sim \exp(-aq^2\sqrt{t})$. The segmental friction coefficient ζ can be calculated from the coefficient of the exponential of decay $S(q^2\sqrt{t})$ from the relation $\zeta/l^2 = k_B T / (3\pi a^2)$, in which l represents the rms size of a polymer segment. From the final results displayed in Figure 3 we obtain

$$\begin{aligned}\zeta/l^2 &= 0.84 \times 10^8 \text{ Nsm}^{-3} \text{ for labelling A;} \\ \zeta'/l'^2 &= 2.55 \times 10^8 \text{ Nsm}^{-3} \text{ for labelling B.}\end{aligned}$$

The decay is slower for the system with labelling B as compared to labelling A. This is in conflict with the standard Rouse model for dynamically homogeneous chains, which predicts that because of dynamic scale invariance the two segmental friction coefficients should be the same.

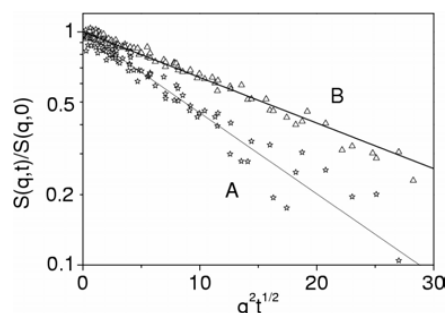


Figure 3. Logarithmic plot of the correlation function for the system with labelling A and B, respectively, at $T = 353$ K. The data is plotted as a function of $q^2\sqrt{t}$, with q represented in nm^{-1} and t in ns.

We attribute the observed slowing down for labelling B to dynamic heterogeneity of the system, which can be understood as follows. For labelling A, the labelled monomers are distributed along the elementary chain. Only small monomers close to the large connecting UPy groups will feel their effect and slow down. The dynamics of the majority of small monomers further way from the bulky groups will not be affected by this effect. In contrast, for the labelling B, due to the fact that the full elementary chain is labelled, the slowing-down effect by the bulky connectors cannot be avoided. Hence by incorporating the larger friction experienced by the bulky UPy groups into the Rouse model, the observed slower relaxation can be rationalized.

A.S. Muresan, J.L.A. Dubbeldam, H. Kautz, M. Monkenbusch, R.P. Sijbesma, P. van der Schoot, W.H. de Jeu: *Dynamic Heterogeneity in Hydrogen-Bonded Polymers*, Phys Rev. E (submitted).



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

Proposal number:	NSE-04-008		
Experiment title:	Low energy spin dynamics in CMR perovskites		
Dates of experiment:	28.02. – 02.03.2005	Date of report:	19 May 2006
Experimental team: Names	Addresses		
F.J.Bermejo P. Romano	Dept. Electricity & Electronics, University of the Basque Country, Bilbao Rutherford Appleton Laboratory, Chilton, Didcot, UK		
Local Contact:	M. Monkenbusch		

Experimental report text body

The experiment was basically a feasibility test aiming to carry out NSE studies on the diffusive spin dynamics on $\text{La}_{0.7}\text{Pb}_{0.3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ ($0 < x < 0.3$) colossal magneto-resistive manganites. Previous data measured on a backscattering instrument (IN10 at ILL) evidenced the presence of diffusive spin dynamics for an iron-doped sample with $x=0.2$ which macroscopically behaves as an unconventional spin-glass.

Results measured on NSE are summarized in the accompanying graphs that depict the time and temperature dependence of the observed relaxation for the above mentioned sample.

Further measurements carried out using the IN11 spectrometer at the ILL gained from the previous experience using NSE and yielded a complete set of relaxation curves.

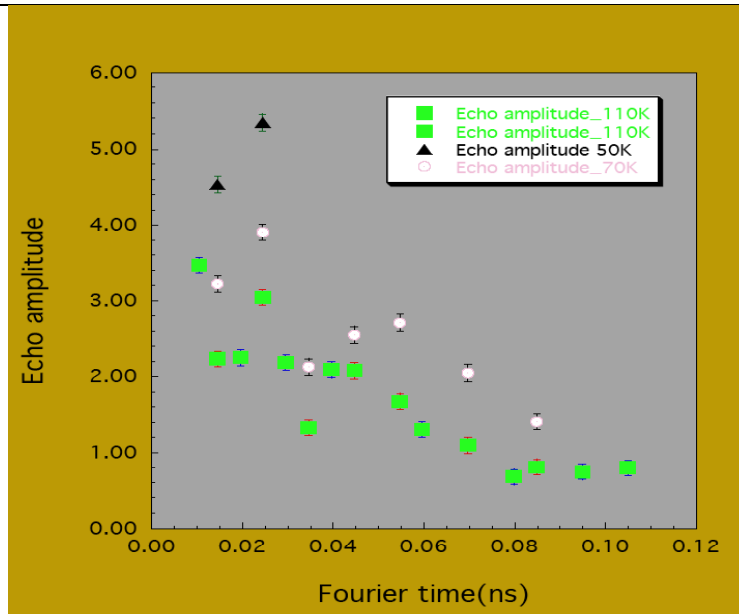


Fig.1 Echo amplitudes for the $x=0.2$ sample and some temperatures.

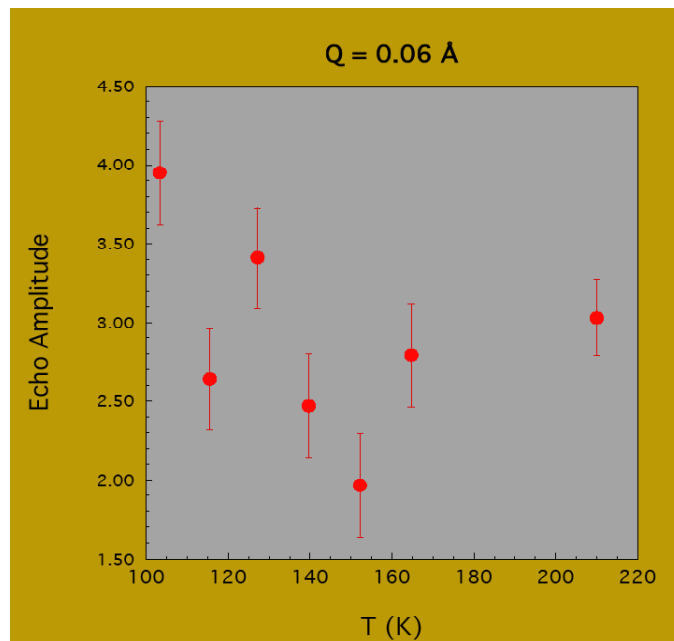


Fig.2 Temperature dependence of the echo amplitude for a fixed value of the momentum-transfer



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

Proposal number:	NSE-04-018		
Experiment title:	Diffusion of methylpentane in silicalite		
Dates of experiment:	15/08-24/08/2004	Date of report:	22/02/2006
Experimental team: Names	Addresses		
H. Jobic	Institut de Recherches sur la Catalyse 2, avenue Albert Einstein 69626 Villeurbanne France		
Local Contact:	M. Monkenbusch		

Experimental report text body

MFI-type zeolites (ZSM-5 and its Al-free analogue silicalite) are amongst the most industrially important zeolites. For example, MFI-type zeolites are used to separate linear from branched alkanes (the branched alkanes are of higher value to increase the octane number of gasoline). In the real processes, there are usually mixtures of several linear and branched alkanes. Predictions are difficult since the reported diffusivities of each component vary in a wide range, despite extensive work. Whereas the diffusion of linear alkanes in silicalite has been studied by several techniques [1], there is much less work on the diffusion of branched alkanes in this zeolitic structure.

The diffusion of isobutane, the simplest branched alkane, has been recently measured by neutron spin-echo (report NSE-02-012). The diffusion of a slightly bulkier molecule: 2-methylpentane, one of compounds obtained from petroleum refining or catalytic cracking, could also be measured on the NSE spectrometer. Intermediate scattering functions were recorded at different Q values and temperatures (e.g. Figure 1). This is the first time that the diffusion of this alkane is characterized by a microscopic method (PFG NMR does not work for this system).

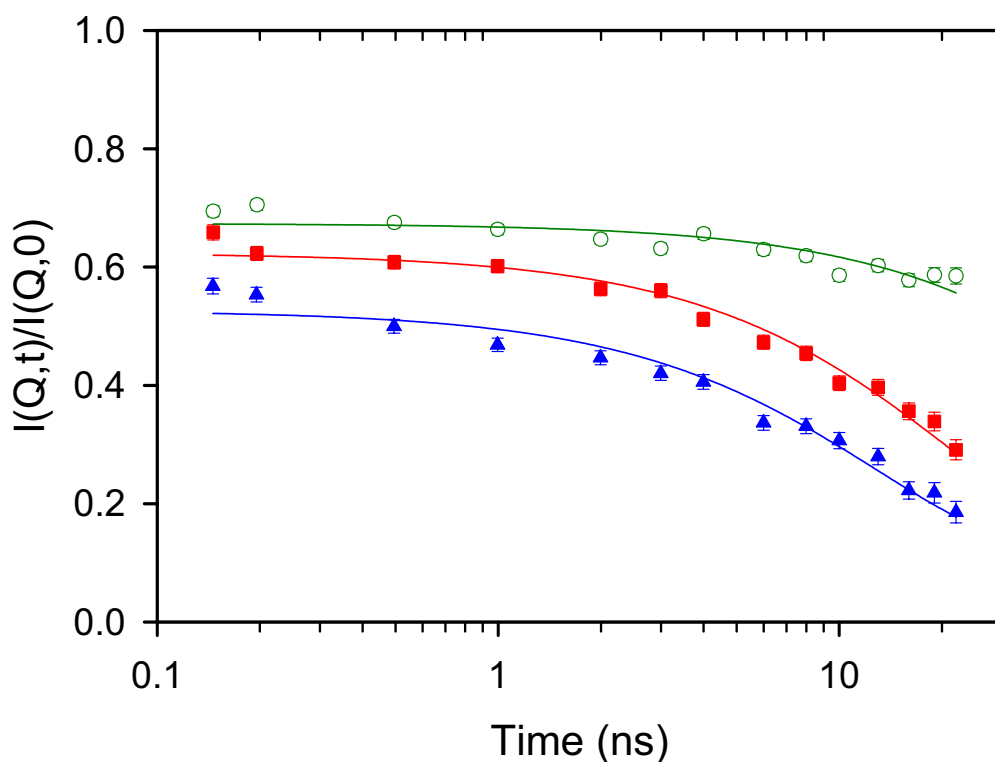


Figure 1. Normalised intermediate scattering functions obtained for 2-methylpentane at 580 K in silicalite, for different Q values: ($\circ$): 0.1, ($\blacksquare$): 0.2, and ($\blacktriangle$) 0.3 $\text{\AA}^{-1}$.

Diffusion coefficients were extracted using a jump diffusion model. The value obtained at 490 K: $3.5 \times 10^{-12} \text{ m}^2\text{s}^{-1}$, is noticeably lower than the diffusivity of isobutane at the same temperature: $2.1 \times 10^{-12} \text{ m}^2\text{s}^{-1}$ (ratios varying from 2 to 20 have been reported in the literature from macroscopic techniques). An activation energy for diffusion could also be estimated: 36 kJ/mol.

Reference

[1] H. Jobic, J. Mol. Catal. A 158 (2000) 135.



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

Proposal number:	NSE-04-019		
Experiment title:	Single-time relaxation dynamics in molecular nanomagnets		
Dates of experiment:	03 March 2005	Date of report:	17/05/2006
Experimental team: Names	Addresses		
Flavio Carsughi	Dipartimento di Scienze Applicate ai Sistemi Complessi (SASC) Universita' Politecnica delle Marche, Via Brecce Bianche I-60131 Ancona Italy INSTITUT FUER FESTKOERPERFORSCHUNG Forschungszentrum Juelich Leo Brand Strasse D-52425 Juelich		
Roberto Caciuffo	Institute for Transuranium Elements Postfach 2340, D-76125 Karlsruhe		
Local Contact:	Michael Monkenbusch		

Experimental report text body

An exploratory experiment was performed to verify the possibility of measuring by neutron spin-echo spectroscopy the long-time decay of the intra-cluster spin-spin correlation functions in a molecular nanomagnet.

The investigated system was a ring-shaped octanuclear cluster, containing 7 Cr ions ($s = 3/2$) and one Mn ion ($s = 5/2$) with antiferromagnetic nearest-neighbor exchange coupling and a spin ground state $S = 1$. Three grams of polycrystalline, partially deuterated material (90% D atoms per cluster) have been used in a standard cryostat.

The NSE spectrometer has been used in its standard mode of operation at fixed Fourier times, between 0.01 and 10 ns. In spite of the high degree of deuteration, hydrogen spin-incoherent scattering was still very high, comparable in magnitude to the nuclear coherent scattering and about a factor 50 more intense than the magnetic signal. Data have been collected with the π flipper removed for a value of the momentum transfer $Q = 0.8 \text{ \AA}^{-1}$ corresponding to minima in the elastic coherent scattering distribution (away from Bragg peaks).

Measurements have been performed at $T = 19$ K, while scanning the Fourier time by varying the precession field in the accessible range. Polarization analysis to normalize the echo amplitude has been performed removing the $\pi/2$ flippers. The results were disappointing. The experiment suffered by low counting rate and bad signal to noise ratio. Although some decay of the spin-spin temporal correlation function has been observed, the quality of the data is such that no substantial conclusions can be reached. The physics addressed is, however, quite interesting and further efforts seems justified. Further experiments should be performed on fully deuterated samples, for Q values where the $S(Q)$ function is not contaminated by Bragg peaks. Furthermore, the echo group should be measured for an extended range of the symmetry coil current to better define the amplitude and the phase of the signal.



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

Proposal number:	NSE-04-022		
Experiment title:	Tuning the structural α -relaxation in Poly(methyl methacrylate) (PMMA) by neutron spin echo		
Dates of experiment:	26/01/2005-02/02/2005	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:	Michael Monkenbusch		

Experimental report text body

With these NSE experiments on fully deuterated poly(methyl methacrylate) (PMMA-d8) we wanted to investigate the temperature dependence of the dynamic structure factor at its first maximum ($Q_{\max} \approx 0.8 \text{ \AA}^{-1}$). With increasing temperature, this first peak in the structure factor $S(Q)$ shows an increase of intensity and shifts towards lower Q -values, suggesting that it mainly reflects interchain correlations. In this way, we would isolate the α -relaxation in a polymer showing a very important contribution of the secondary relaxation as studied by other techniques [1].

With a wavelength of $8 \text{ \AA}$ and by using the furnace we have investigated a temperature range between the glass transition temperature T_g ($T_g = 400 \text{ K}$) and $\approx 500 \text{ K}$. TiZi was used to determine the resolution function at the same Q -value. As can be seen in Fig. 1, a decay of the dynamic structure factor is observed for all temperatures investigated, even at the glass transition; there, however, the dynamics of the α - or structural relaxation should be too slow to lead to a decay of the interchain correlations in the NSE dynamic window. For this reason a further measurement on the sample was performed at 300 K . Even at such low temperature, clearly in the glassy state, a non negligible decay was observed (see Fig. 1).

The relaxation times have been obtained from a fit of the NSE data by Kohlrausch-Williams-Watts (KWW) functions $S(Q,t) \propto \exp[-t/\tau(T)]^\beta$ with a stretching exponent β of 0.5. The descriptions delivered can be seen in Fig. 1. Figure 2 shows the temperature dependence of the so obtained time scales $\tau(T)$. Well above T_g the times follow the behaviour expected for the α -relaxation as observed from spectroscopic techniques (DS) [1]. Below 450 K , strong deviations with respect to such temperature dependence become evident.

This phenomenon reminds the decoupling of timescales reported for 1,4-polybutadiene at the first minimum of $S(Q)$ [2], that was later interpreted in terms of the merging of the α - and β -relaxations in that polymer [3]. However, such a scenario would not explain our NSE results on PMMA, since they have been obtained at the first peak, where the contributions from secondary relaxations should be strongly suppressed [3].

These astonishing results suggest that either the resolution function of the NSE instrument changes from the PMMA-d8 to the TiZi measurements (e.g. due to a small change in the sample size) or that indeed a relaxational process different from the α -process –a secondary relaxation- leads to the decay of the correlations at the first peak in this polymer. It is of utmost importance to clarify this question by checking the results on the low temperature measurements with an independent experiment.

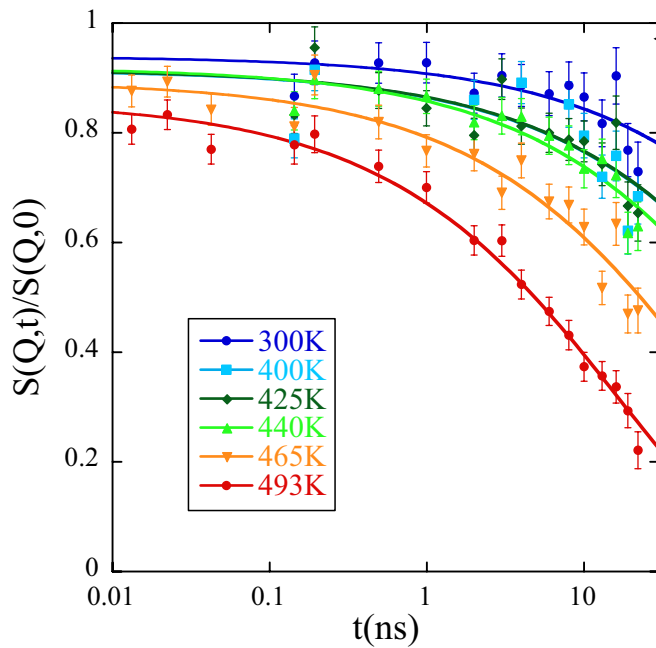
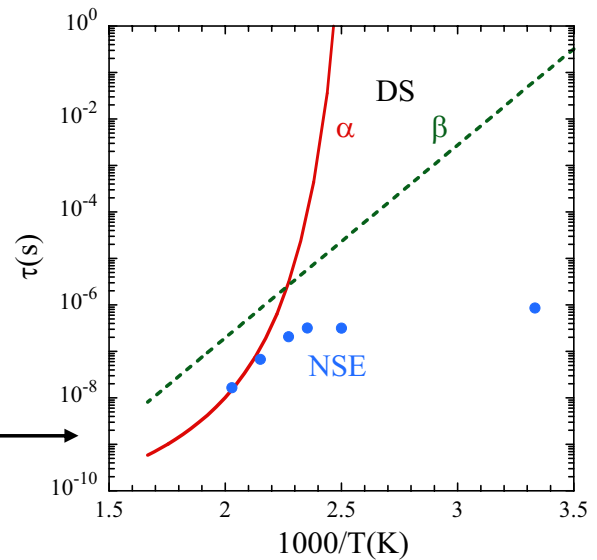


Figure 1: Dynamic structure factor measured by NSE on a fully deuterated PMMA sample at the first maximum ($0.8\text{\AA}^{-1}$) and the temperatures indicated. The solid lines are fits with KWW functions with $\beta=0.5$.

Figure 2: Arrhenius plot of the relaxation times obtained from these NSE measurements (circles) and those by dielectric spectroscopy for the α - (solid line) and β -relaxations (dotted line) [1].



References

- [1] R. Bergman, F. Alvarez, A. Alegría and J. Colmenero, J. Chem. Phys. **109**, 7546 (1998)
- [2] D. Richter, R. Zorn, B. Farago, B. Frick and L. J. Fetters, Phys. Rev. Lett. **68**, 71 (1992)
- [3] A. Arbe, D. Richter, J. Colmenero, B. Farago, Phys. Rev. E **54**, 3853 (1996)



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

Proposal number:	NSE-04-024		
Experiment title:	Chain dynamics of a short 1.5kg/mol PE chain in a long matrix		
Dates of experiment:	May 2005	Date of report:	15.5.2006
Experimental team: Names	Addresses		
M. Monkenbusch M.Zamponi A.Wischnewski	IFF, FZ Juelich		
Local Contact:	M. Monkenbusch		

Experimental report text body

In the reptation model for long chain polymer melts the topological constraints due to entanglements are described by a virtual tube which follows the primitive path of the observed test chain. However, this definition means, that a test chain with a length in the order of one entanglement distance can not be captured in a tube. This conclusion does not depend on the matrix properties and holds even if the matrix chains are much longer than the test chain.

For a short chain with a length in the order of one entanglement length (M_e) in a long matrix therefore free Rouse behaviour is expected. A previous measurement (NSE_04_015) of labeled 2.5kg/mol polyethylene (PE) chains in a long chain (36kg/mol) PE matrix revealed deviations from the expected Rouse behaviour. The chain length was slightly above the entanglement length ($M_e=2\text{kg/mol}$ for PE). Therefore now the dynamic structure factor of a 1.5kg/mol PE chain in the same long matrix has been measured.

The experiments have been performed at a temperature of 509K (as before), covering a momentum transfer range from 0.5nm^{-1} to 0.96nm^{-1} . The data were corrected for resolution and background, latter estimated from a fully deuterated sample of the matrix chains.

In comparison to the 2.5kg/mol chain the dynamic of the 1.5kg/mol chain is considerably faster but still do not follow the expected Rouse behaviour (fig.1). Comparing the data to the Rouse function with known Rouse rate (solid lines), a strong slowing down of the dynamic is observed. Also by fitting the Rouse rate the data cannot be described. If the fit is limited to times below the entanglement time (7ns) the short time range agree with the Rouse model (dashed lines) but at longer times the dynamic is significantly slower. Although the chain is below the entanglement length and therefore should not be object of topological constraints the deviation of the dynamic structure factor indicates that the short chain is captured in the tube built by the long chain matrix.

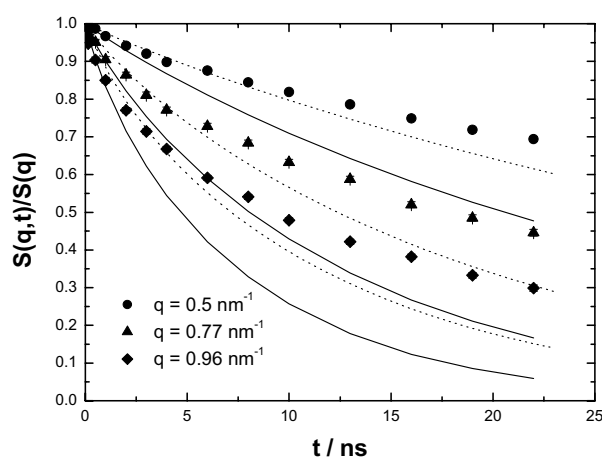


Fig.1: Dynamic structure factor of a h-1.5kg/mol chain in d-36kg/mol matrix. Q-values as indicated in the plot.
Lines: solid Rouse expectation, dashed Rouse fit.

For the lowest q-value the center of mass diffusion dominates and internal modes are negligible so that the center of mass mean squared displacement can be extracted (fig.2). For a free Rouse diffusion a linear time dependence of the mean squared displacement is expected, whereas the data show a clear subdiffusive motion ($\langle r^2 \rangle \sim t^{0.7}$). This again points to the surprising result that the short chains, although they are below M_e , can not move freely.

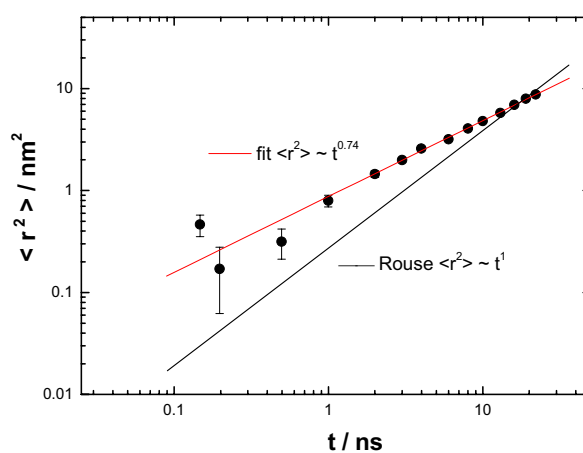


Fig.2: Center of mass mean squared displacement for $q=0.5\text{nm}^{-1}$ for the h-1.5kg/mol chain in the long chain matrix.
The black line shows the Rouse expectation of normal diffusion, the red line is a fit of the data.



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

Proposal number:	NSE-05-001		
Experiment title:	Dynamics of glass forming liquids in the low-Q range. A direct comparison between a low molecular mass glass former and the polymer counterpart.		
Dates of experiment:	16-05-05 to 29-05-05 and 06-06-05 to 13-06-05	Date of report: 03-10-2005	
Experimental team: Names	Addresses		
1. Ángel Alegría 2. Madhusudan Tyagi 3. Arantxa Arbe	Física de Materiales, Facultad de química, Apdo. 1072, 20080 San Sebastián, SPAIN Donostia International Physics Center, 20018, San Sebastián, SPAIN Unidad Física de Materiales (CSIC-UPV/EHU), Apartado 1072, 20080 San Sebastián SPAIN		
Local Contact:	M. Monkenbusch		

Experimental report text body

This work was carried out to examine the dynamics of trimer of vinyl acetate (3VA) which is a short chain counterpart of poly(vinyl acetate). The dynamics of polymeric systems and low molecular weight glass formers (GFL) share some universal features and have been paid lot of attention recently¹⁻³. Typically, in GFL and polymeric systems one observes so-called anomalous sub-linear diffusive regime below $Q=1\text{\AA}^{-1}$ which is revealed in time dependence of intermediate scattering function $S(Q,t)$ as $\sim t^{-\beta}$. This is also reflected in Q -dependence of characteristic times as $\tau \sim Q^{-2/\beta}$. This anomalous diffusive regime continues down to very low Q values where finally, one expects the dynamics of GFL is to be dominated by center of mass diffusion of entire molecule which should be reflected in a simple exponential time decay of $S(Q,t)$. In this simple diffusive regime momentum transfer dependence of characteristic times also becomes weaker and is given by $\tau \sim Q^{-2}$. On the contrary, one expects a crossover to Rouse dynamics in polymeric systems at low Q -values because of their chain connectivity. Our measurements on 3VA were made keeping this objective in mind.

The experiments were carried out on a fully protonated 3VA sample at 350K in order to get characteristic time scales in the window of NSE. The scattering functions were measured at 4 different Q -values viz. 0.08, 0.14, 0.20 and $0.28\text{\AA}^{-1}$. The wavelength of the incoming neutron beam was set to $8\text{\AA}$. As NSE signal strength in incoherent samples is weak because $2/3^{\text{rd}}$ of the sample intensity is converted to background, each Q value was measured over a period of two days for 10 Fourier times to get good statistics. The sample was taken in a rectangular aluminium container of 5cm by 5cm size. As multiple scattering effects are efficiently suppressed, sample thickness was chosen to be 0.5mm which resulted in a transmission of close to 50% and increased very much needed intensity. In addition, empty container was measured at all the Q -values under identical conditions. The resolution of the instrument was also measured at different Fourier times using carbon powder.

Fig.1 represents all incoherent intermediate scattering functions measured at different Q values. The good quality of experimental points can be seen from low error bars in this figure. The scattering functions are fitted to stretched exponential function, $S(Q,t) \sim \exp\{-(t/\tau)^\beta\}$, where τ is the characteristic time. The characteristic times so obtained are shown in Fig.2 where in double logarithmic plot relaxation times are plotted against Q . The presence of anomalous diffusive regime at higher Q values is apparent through stretched exponential behaviour of $S(Q,t)$. It can also be seen that all the three higher Q values can be described coherently with the same stretching parameter (which is deduced from the master curve of these Q -values). The characteristic time scales at the higher Q values follows a power law in momentum transfer dependence in the form of $\tau = \tau_0 Q^{-2/\beta}$ which is typically the case for a glass former as mentioned above.

However, a clear single exponential time decay of scattering function can be seen at lowest Q value measured in our experiments which is also shown in Fig.1 along with all other Q -values. Interestingly, a clear deviation of characteristic time from the trend followed by higher Q -values can be seen in Fig.2. Simple exponential behaviour of $S(Q,t)$ followed by weaker momentum transfer dependence of characteristic time clearly shows that a crossover to simple diffusive-like mechanism takes place in our sample somewhere between 0.14 and $0.08 \text{ \AA}^{-1}$.

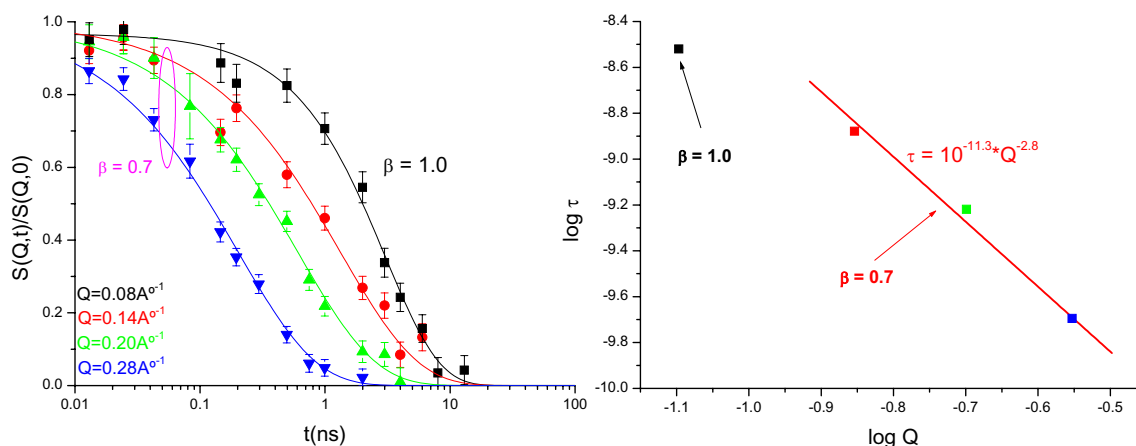


Fig.1: Incoherent intermediate scattering functions at different Q values. The solid lines are fits to stretched exponential function with β values shown in figure.

Fig.2: A double logarithmic plot of characteristic times derived from fitting of scattering function against momentum transfer Q .

References:

- [1] Wayne L. et al. *Macromolecules* **37** (2004) 4711
- [2] Yifu Ding, et al *Macromolecules* **37** (2004) 9264
- [3] L. Goitiandia, A. Alegría, *Journal of Chemical Physics* **121** (2004) 1636



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

Proposal number:	NSE-05-004		
Experiment title:	Tuning the structural α -relaxation in Poly(methyl methacrylate) (PMMA) by neutron spin echo – Checking low T-contributions		
Dates of experiment:	24/04/2005-26/04/2005	Date of report:	28/11/2005
Experimental team: Names	Addresses		
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:	Michael Monkenbusch		

Experimental report text body

The aim of this experiment was to clarify previous NSE results obtained by us on fully deuterated poly(methyl methacrylate) (PMMA-d8) ($T_g \approx 400\text{K}$) [1]. In that work [1], we had measured the dynamic structure factor $S(Q,t)$ at its first maximum ($Q_{\max} \approx 0.8\text{\AA}^{-1}$) in the temperature range between room temperature (RT) and 500K. TiZr was used to determine the resolution function at the same Q-value. Our goal was to tune the α -relaxation of PMMA and to investigate whether or not it follows the general trend observed in more simple polymers like polyisoprene or polybutadiene. As can be seen in Fig. 1, a decay of $S(Q_{\max},t)$ was observed for all the temperatures investigated and, surprisingly, even at 300K, which corresponds to the glassy state in PMMA. There, however, it is clear that the α -relaxation can not be responsible for any decay of the correlations in the dynamic window of NSE. Then they are only two possibilities: i) the resolution function changes from the PMMA-d8 to the TiZr measurements or ii) a relaxational process different from the α -relaxation (like maybe the β -relaxation) leads to the decay of the intermolecular correlations in this polymer (note that it would be quite an unexpected behavior).

That's why, in order to understand this intriguing question, we have measured the same sample at RT and 50K in the cryostat. Both spectra were indistinguishable within the experimental uncertainties. Since at 50K, the scattering of the sample should be completely elastic (note that the tunneling of the ester methyl group does not lead to quasi-elastic broadening in the coherent case), we can conclude that the observed decay is due to our first hypothesis and the resolution function determined by the TiZr sample is inappropriate to correct our previous results [1].

References:

[1] C. Genix et al., Experimental Report NSE-04-022

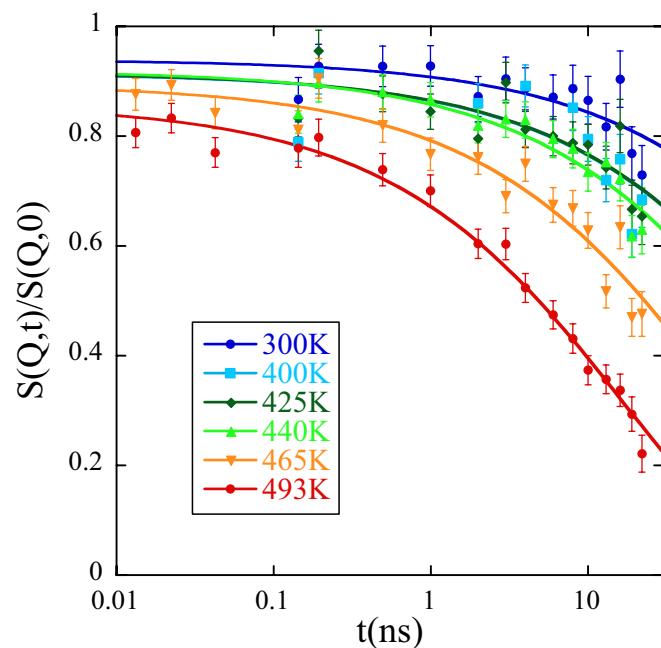


Figure 1: Dynamic structure factor measured by NSE [1] on a fully deuterated PMMA sample at the first maximum ($0.8\text{\AA}^{-1}$) and the temperatures indicated. The solid lines are fits with KWW functions with $\beta=0.5$. The results of the present experiment show that these data have to be rechecked, since no decay of the structure factor is really observed at 300K.



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

Proposal number:	NSE-05-005		
Experiment title:	PEO chain dynamics in a PEO-PMMA blend		
Dates of experiment:	04.04-20.04.2005	Date of report:	29.11.2005
Experimental team: Names	Addresses		
Katarzyna Niedzwiedz	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Andreas Wischnewski	IFF, Forschungszentrum Jülich, 52425 Jülich		
Prof. Dr. Dieter Richter	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Michael Monkenbusch	IFF, Forschungszentrum Jülich, 52425 Jülich		
Local Contact:	Dr. Michael Monkenbusch Dr. Ralf Biehl		

Experimental report text body

Dynamics in polymer blends is a very attractive field of research. 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.

This work was motivated by unexpected NMR results reported by Lutz et al. [1] on a miscible PMMA/PEO blend, a system with widely separated glass transitions ($T_g^{\text{PEO}} \approx 210$ K, $T_g^{\text{PMMA}} \approx 400$ K). Lutz found that the PEO dynamics appears to be completely decoupled from the PMMA motions, e.g. at the glass transition of PMMA the PEO motion in terms of the rotational autocorrelation function is 12 orders of magnitude faster than that of PMMA. Apparently, the PEO chain can relax locally as if it was embedded in a PEO melt rather than a solid PMMA matrix.

We have investigated two samples with 25% PEO in a matrix of 75% deuterated PMMA. In the first case, for a fully protonated PEO component, the measurement was performed at $T = 375$ K for Q-values of 0.05, 0.08, 0.10, 0.14, 0.17 and $0.20 \text{ \AA}^{-1}$. This sample has contrast only between the protonated PEO chains and the deuterated PMMA matrix, which is stiff at this temperature. Therefore we see no dynamic signal of the sample, the NSE response is purely elastic (fig. 1).

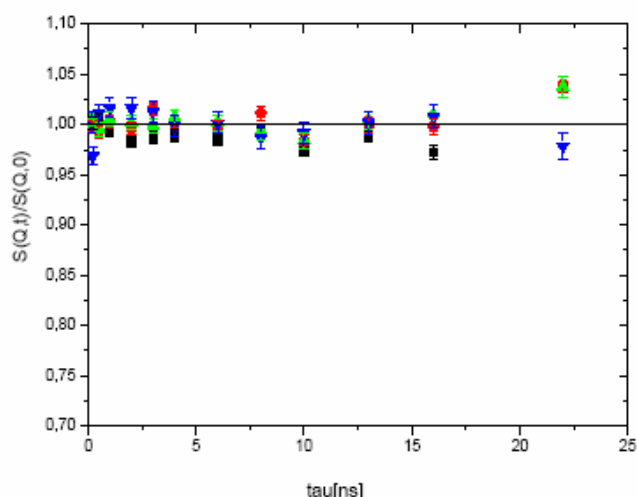


Fig. 1 The intermediate scattering function $S(Q,t)/S(Q,0)$ obtained for a PEO/PMMA blend system (25% h-PEO and 75% d-PMMA) at $T = 375$ K and for different Q -values: $Q = 0.05 \text{ \AA}^{-1}$ (squares), $Q = 0.08 \text{ \AA}^{-1}$ (circles), $Q = 0.10 \text{ \AA}^{-1}$ (triangle up), $Q = 0.14 \text{ \AA}^{-1}$ (triangle down). The solid line at $S(Q,t)/S(Q,0) = 1$ is a guide for the eye.

The second sample was composed of 12.5 % h-PEO and 12.5 % d-PEO in the deuterated PMMA matrix. Here, the protonated PEO chains have a dynamic contrast to the deuterated PEO chains, the PEO dynamics becomes visible by NSE. Measurements were done at three different temperatures ($T = 370$ K, 400 K and 430 K) at $Q = 0.20 \text{ \AA}^{-1}$, $Q = 0.28 \text{ \AA}^{-1}$ and $Q = 0.36 \text{ \AA}^{-1}$. Moreover at $T = 400$ K also lower Q -values ($Q = 0.08 \text{ \AA}^{-1}$, $Q = 0.14 \text{ \AA}^{-1}$ and $Q = 0.17 \text{ \AA}^{-1}$) have been measured. The results for $T = 400$ K are compared to the scattering function of pure PEO at the same temperature in fig. 2. The dynamics for PEO in the blend is significantly slower than for the pure PEO system.

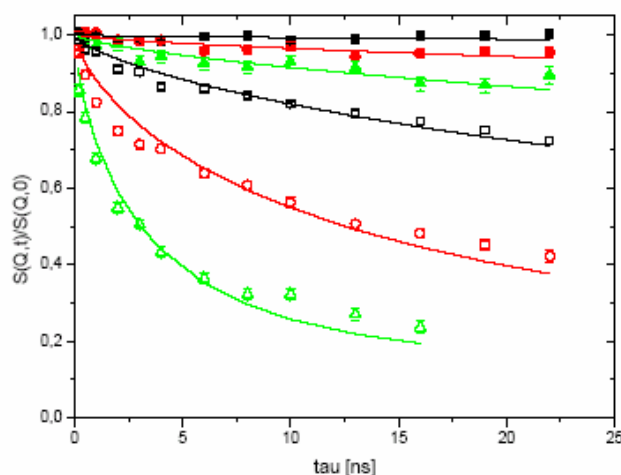


Fig. 2 Neutron spin echo data obtained for PEO (10% h-PEO in a d-PEO matrix, open symbols) compared to PEO in the blend (12.5% h-PEO, 12.5% d-PEO and 75% d-PMMA, full symbols) at $T = 400$ K. Squares correspond to data at $Q = 0.10 \text{ \AA}^{-1}$, circles to $Q = 0.15 \text{ \AA}^{-1}$ and triangles to $Q = 0.20 \text{ \AA}^{-1}$. Solid lines are guides for the eye.

[1] T.R. Lutz et al., *Macromolecules*, 36, 1724 (2003)



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

Proposal number:	NSE-05-007		
Experiment title:	Confinement effects of diblock copolymers in bicontinuous microemulsions – A dynamic study		
Dates of experiment:	23.06.2005	Date of report:	28.06.2006
Experimental team: Names	Addresses		
Simona Maccarrone Henrich Frielinghaus	Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich		
Local Contact:	Olaf Holderer		

Experimental report text body

Microemulsions are thermodynamically stable and macroscopically homogeneous mixtures of two non miscible components like oil and water mediated by surfactant molecules. Under certain conditions of temperature and surfactant concentration, oil and water result completely mixed (1 phase region) and the minimum quantity of surfactant requested to solubilize equal amounts of oil and water is a measure for its “efficiency”. Recently, it was found out that the addition of amphiphilic diblock copolymer can increase enormously the efficiency of the emulsification capacity of non ionic surfactants (boosting effect). Microscopically we have the monolayer of surfactant separating domains of oil and water. From a previous work done by Endo it was shown that the polymer decorates the membrane increasing its stiffness.

The Helfrich theory describes the elastic properties of the surfactant membrane to be dominating. The bending rigidity κ is the modulus of the mean curvature and by the Gaussian random field theory we are able to get this energetical parameter from a relationship involving the domain spacing d and the correlation length ξ . These two structural parameters are easily obtained from small angle neutron scattering (SANS) measurements.

Computer simulations by Auth initially came up with the idea, that polymer confinement could play a role in microemulsions. The simulations focus on anchored diblock copolymers. For low confinement the theoretical values were confirmed. At intermediate confinement the sensitivity of the polymer effect is increased due to the higher presence of the polymer at the interface. At very high confinement the diblock copolymer effect could be reversed to anti-boosting since then the anchoring does not play a role anymore and the entropy of a flat polymer is highly unfavourable. Our task was to verify and quantify eventually the maximum polymer boosting.

Several bicontinuous microemulsions were studied intensively rendering the domain size d comparable to the polymer size (R_g). Two symmetric diblock copolymers PEP₂₂-PEO₂₂ and PEO₁₀-PEO₁₀ were chosen. The domain spacing of the microemulsions was varied by the use of different oils (hexane, octane, decane,

dodecane, tetradecane) influencing the efficiency primarily. Experimentally we found at relatively large d/R_g where the confinement is weak, the sensitivity of the polymer boosting effect unchanged. With increasing confinement (d/R_g closer to 1) the sensitivity is only slightly enhanced, and finally a strongly reversed behaviour (anti-boosting) is observed. The behaviour at medium confinement shows a much lower sensitivity compared with the theory of Auth. This enhancement would have been very interesting for applications, while the reversed behaviour could be an explanation how red blood particles could sneak into small vessels.

After the structure of such microemulsions has been determined by SANS, we performed neutron spin-echo (NSE) experiments that is a well-suited method for studying the dynamic properties of microemulsions, since the Fourier time range of this technique matches with the characteristic time range of the membrane dynamics. This technique allows the direct determination of the “bare” (not renormalized) bending rigidity and changes due to the confinement of the diblock copolymers.

In this case the membrane bending rigidity is obtained by numerically integrating $S(q,t)$ from the Zilman-Granek theory. The bending modulus is the only free fitting parameter. Our intention was to compare finally this bare membrane bending modulus to the renormalized one as obtained from SANS.

The NSE experiments have been carried out on the length scales of the confinement, where the theoretical maximum occurred. We performed the experiments in film contrast, i. e. with deuterated decane and dodecane, deuterated water and protonated surfactant and polymer (PEP₂₂-PEO₂₂). For both oils we prepared samples with and without added diblock copolymer at the same surfactant concentration, thus giving a direct access to the changes induced by the diblock copolymers.

From preliminary observations the relaxation time of the polymer doped microemulsion is faster than for the equivalent pure microemulsion. For example, in the case of decane, plotting the ratio of the NSE spectra relative to the system with and without polymer, we can observe a first comparison (see fig. 1). The variation of decay in time is visible for medium and high q while nothing almost changes for low q -values. Moreover from preliminary fittings no variation for the bending rigidity in the case of C10 is found while a decrease is obtained for dodecane. Everything in agreement with the previous SANS experiments. Anyway further more precise analysis are in progress.

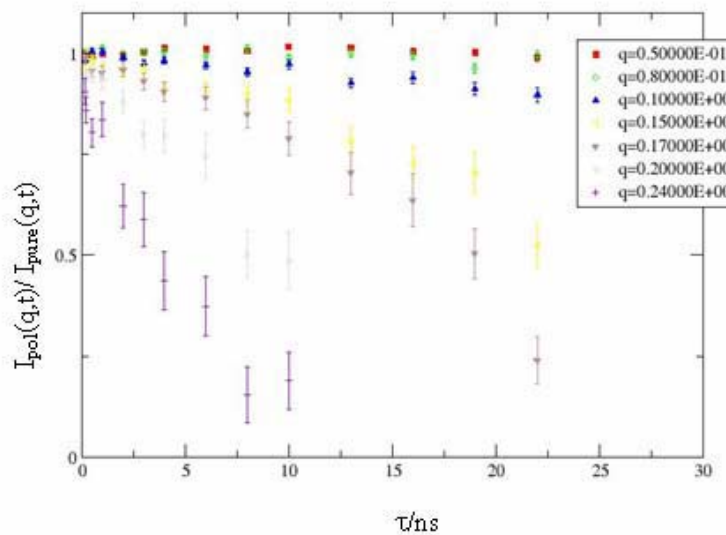


Figure 1. Ratio between NSE spectra for different q (nm^{-1}) values relative to decane-samples with and without polymer vs. time.



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

Proposal number:	NSE-05-008		
Experiment title:	High Q dynamic structure factor of PEO		
Dates of experiment:	13.06-25.06.2005	Date of report:	29.11.2005
Experimental team: Names	Addresses		
Katarzyna Niedzwiedz	IFF, Forschungszentrum Jülich, 52425 Jülich		
Dr. Andreas Wischniewski	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. Michael Monkenbusch Dr. Ralf Biehl		

Experimental report text body

Recent studies of a PEO / PMMA polymer blend by neutron spin echo spectroscopy (NSE-05-005) and backscattering (BSS-05-008) in Jülich revealed surprising results: At temperatures below and around the glass transition temperature T_g of the stiff PMMA matrix ($T_g \approx 400$ K) the dynamics of the low T_g component PEO ($T_g \approx 200$ K) is fast but restricted to small volumes of about 1 nm (confinement). Furthermore, the collective dynamics of PEO (as determined by NSE at lower Q) appears to be significantly slower compared to the self-motion as measured by BSS.

The observed behaviour resembles effects of a tube confinement in long entangled polymer melts, however, with unexpected (and probably unphysical) parameters for the reptation model.

The aim of this experiment was to compare the deviations of the PEO dynamics in a PEO/PMMA blend from the Rouse behaviour to the dynamics of the chains in the pure PEO system. Since the molecular weight is several times longer than the entanglement distance, it is expected that in the pure PEO system we will observe deviations from the Rouse model, which are due to entanglements and can be explained in the framework of the reptation model.

The investigated PEO chains had the same molecular weight as the one used in the PEO/PMMA blend ($M_w = 24$ kg/mol). To measure the coherent single chain dynamic structure factor a sample with 10% pratonated-PEO and 90% deuterated-PEO was used. The wavelength of the incoming neutrons was $8 \text{ \AA}$, the temperatures were $T = 350\text{K}, 375 \text{ K}, 400 \text{ K}, 430 \text{ K}$ and the momentum transfer was $0.05 \text{ \AA}^{-1} < Q < 0.30 \text{ \AA}^{-1}$. The data were corrected for resolution (graphite) and background (fully deuterated PEO).

An example for the obtained intermediate scattering function $S(Q,t)/S(Q,0)$ for PEO at $T = 375$ K is shown in fig. 1. The data were fitted with the Rouse model at short times up to 5 ns, with the friction coefficient as a free parameter. One clearly sees the deviations from the model at longer times as expected for long chain polymer melts.

However, to fully explore the reptation regime one has to perform this experiment with entirely entangled PEO chains (higher molecular weight) and at Fourier times up to at least 100 ns.

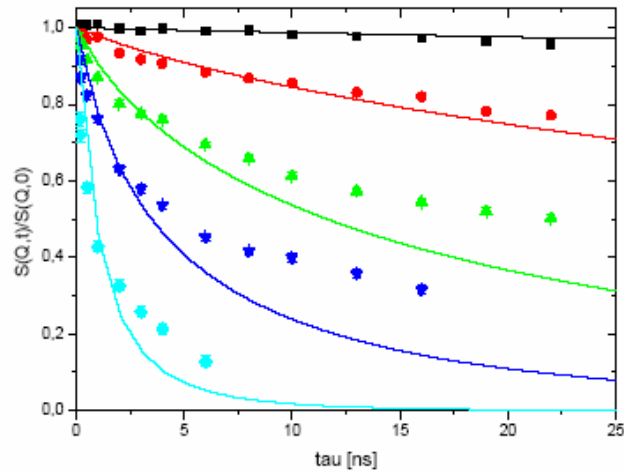


Fig. 1 Dynamic structure factor of PEO at $T = 375$ K, black squares corresponds to data at $Q = 0.05 \text{ \AA}^{-1}$, red circles - $Q = 0.10 \text{ \AA}^{-1}$, green triangles $Q = 0.15 \text{ \AA}^{-1}$, dark blue triangles $Q = 0.20 \text{ \AA}^{-1}$ and light blue diamonds $Q = 0.30 \text{ \AA}^{-1}$. Solid lines represent a fit with the Rouse model restricted to short times (from 0 to 5 ns).



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

Proposal number:	NSE-05-009		
Experiment title:	Cooperative dynamics in short chain polymers		
Dates of experiment:	26.08.-31.08.2005	Date of report:	16.05.2006
Experimental team: Names	Addresses		
M.Zamponi R.Biehl A.Wischnewski	Institut für Festkörperforschung, Forschungszentrum Jülich GmbH Institut für Festkörperforschung, Forschungszentrum Jülich GmbH Institut für Festkörperforschung, Forschungszentrum Jülich GmbH		
Local Contact:	R.Biehl, M.Monkenbusch		

Experimental report text body

Recent experiments of short chains below the entanglement length in a long chain matrix revealed anomalous diffusion behaviour of the short chains (NSE-04-024). Although per definition the short chains should not be affected by the matrix chains and therefore should be able to diffuse freely, the center of mass mean squared displacement showed a clear subdiffusive regime. Apparently the short chains are subject to topological constraints or cooperative dynamics.

Diluting the matrix by adding a small number of oligomer it is expected that the anomalous diffusion of the short chains is influenced. Therefore the mixture as used before (10% labeled (protonated) 1.5kg/mol polyethylene (PE) chains in a deuterated 36kg/mol PE matrix) has been diluted by adding 20% oligomer (nonadecane). Unfortunately sample preparation turned out to be difficult since the oligomer did not precipitate. The solvent therefore had to be evaporated after mixing.

The dynamic structure factor has been measured under the same conditions as before: at a temperature of 509K for 3 different q-values, covering a momentum transfer range from 0.5nm^{-1} to 0.96nm^{-1} . The background correction was estimated from a fully deuterated sample of the matrix chains which was also diluted by 20% oligomer.

In fig.1 the dynamic structure factor of the diluted blend is shown in comparison to the undiluted sample. The observed difference is very small, the dynamics of the diluted sample tends to be somewhat faster, in agreement with the expectation. For the lowest q-value the center of mass mean squared displacement can be extracted from the dynamic structure factor, but apparently also the anomalous diffusion behaviour has not changed.

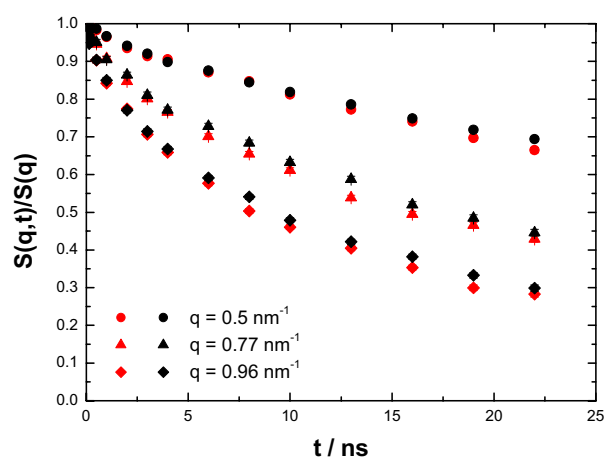


Fig.1: Dynamic structure factor of the diluted h-1.5kg/mol chain in d-36kg/mol matrix (red symbols) in comparison to the undiluted mixture (black symbols). Q-values as indicated in the plot.

A chemical analysis of the diluted sample after the measurement showed that not as much oligomer as expected was in the blend. Instead of the prepared 20% only about 5% oligomer was found. While heating under vacuum during the sample preparation also most of the oligomer must have evaporated. The small amount of remaining oligomer explains that there is only a small difference in the dynamic structure factor visible and that the dynamics is hardly influenced by the dilution.



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

Proposal number:	NSE-05-010		
Experiment title:	Anomalous diffusion in short chain polymer melts		
Dates of experiment:	19.09-26.09.2005	Date of report:	22.05.2006
Experimental team: Names	Addresses		
M.Zamponi R.Biehl A.Wischnewski	Institut für Festkörperforschung, Forschungszentrum Jülich		
Local Contact:	R.Biehl, M.Monkenbusch		

Experimental report text body

Experiments of short chains in a long chain matrix have shown that although the short chains are below or about the entanglement length they are subject to topological constraints (NSE_04_024). The dynamic structure factor followed not the expected Rouse behaviour but was considerably slowed down. For such short chains the center of mass mean squared displacement can be extracted from the measured coherent dynamic structure factor at low wave vectors q . These didisperse blends show a clear subdiffusive regime at earlier times, again illustrating the influence of the topological confinement from the matrix chains.

A previous measurement of a short chain in a short matrix of the same molecular weight still showed deviations from the expected Rouse dynamics and a similar subdiffusive regime was found. The molecular weight (2.5kg/mol) was slightly above the entanglement length ($M_e=2\text{kg/mol}$), therefore in this experiment a short chain in a short matrix below M_e (1.5kg/mol) has been investigated by neutron spin echo spectroscopy. The sample consists of 10% protonated polyethylene (PE) chains with a molecular weight of 1.5kg/mol in a deuterated matrix of the same length. The experiments have been performed at a temperature of 509K at a wavelength of $8\text{\AA}$, covering a q -range of $0.5\text{-}1.0\text{ nm}^{-1}$. The data have been corrected for resolution and background, latter estimated from a fully deuterated sample.

The resulting dynamic structure factor is displayed in fig.1. The data follows qualitatively Rouse dynamics (lines), but quantitatively the fitted Rouse rate deviates from the expectation. The apparent Rouse rate is much lower than the known literature value for PE. This is due to a significant slower diffusion than the Rouse expectation. If the diffusion is fitted separately for the lowest q -value, where internal Rouse modes are negligible, the value is nearly a factor 2 smaller. Fixing this diffusion constant and fitting the data again with the Rouse model for all q 's, the right segmental friction, which determines the Rouse rate, is obtained.

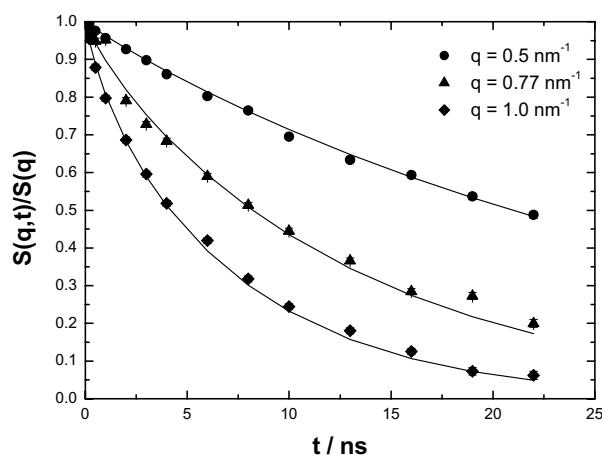


Fig.1: Dynamic structure factor of the 1.5kg/mol homopolymer melt, q -values as indicated in the plot. Lines are a fit with the Rouse model.

For the lowest q -value the center of mass mean squared displacement can be extracted (fig.2). Only at very short times a slight deviation from the expected linear time dependence of normal diffusion is visible. Following the approach by Guenza (M. Guenza, *Macromolecules* **35**, 2714 (2002)) these deviations are due to intermolecular interactions and are expected to slow down the dynamics for times below the Rouse time of the chain. This is consistent with the experimental finding here. The Rouse time of the 1.5kg/mol chain is 4 ns, below this time the deviation from the Rouse expectation is evident.

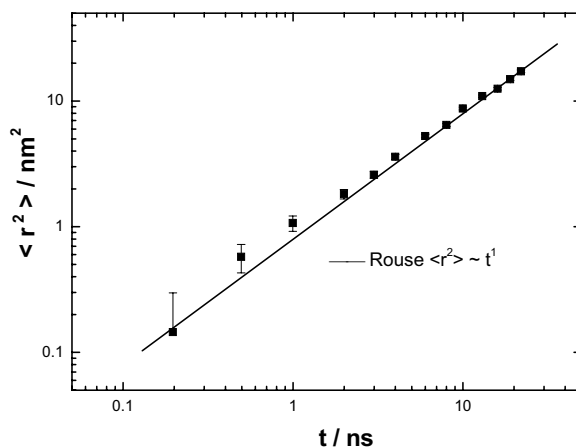


Fig. 2: Center of mass mean squared displacement for $q=0.5 \text{ nm}^{-1}$. The black line shows the Rouse expectation of normal diffusion.