ESRF	**Experiment title:** Concentration fluctuations and alpha-relaxation in binary glass formers	**Experiment number**: SC-2557
Beamline: ID10A	**Date of experiment**: from: 12/11/2008 to: 17/11/2008	**Date of report**: 18/02/2009
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Names and affiliations of applicants (* indicates experimentalists):

Sebastian Schramm*, Dr. Thomas Blochowicz*, Emmanuel Gouirand*, Prof. Dr. Bernd Stühn,

Institut fuer Festkoerperphysik, Technische Universitaet Darmstadt, Germany

Preliminary Report:

The aim of this project was to detect concentration fluctuations and the alpha-relaxation in a binary glass forming system by X-ray Photon Correlation Spectroscopy (XPCS). The experiment was performed in beamline ID10A in SAXS geometry using a partially coherent 8 keV X-ray beam. The fluctuating signal scattered from the sample in a thin capillary was detected by the MEDIPIX detector and subsequently the time correlation-function was calculated for different scattering vectors *q*. The provided 2-dimensional MEDIPIX detector enabled us to do multi speckle XPCS and improve the signal to noise ratio enormously as compared to [Duf02]. The sample investigated was a concentrated polymer solution of oligomeric Poly(-Methylmethacrylate) (PMMA) in Methyl-Tetrahydrofurane (MTHF), which is particularly qualified for XPCS due to the large contrast in electron densities of about 100 el/nm^3. Samples with different molecular weight of PMMA (3 kg/mol and 15 kg/mol) and different concentrations (50 % and 60 % polymer) were analysed.

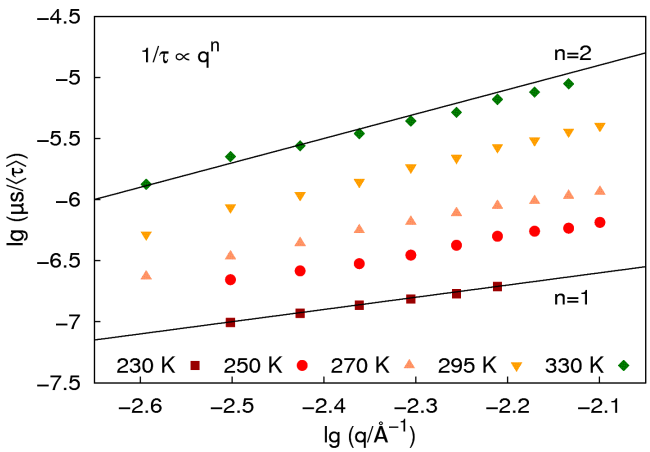

Fig. 1: *Double-logarithmic plot of relaxaton times vs. scattering vector for different temperatures*

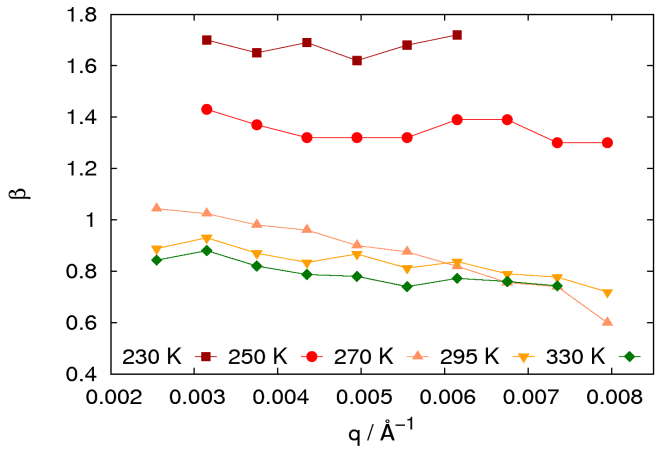

Fig. 2: *KWW streching-exponent vs. scattering vector for different temperatures*

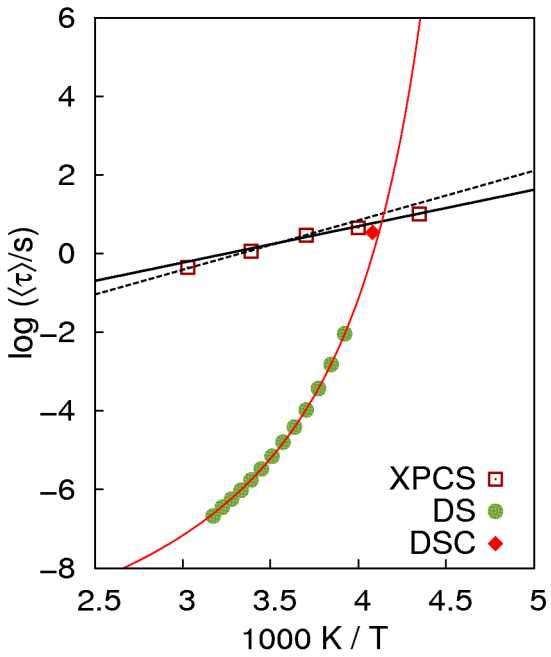

Fig. 3: *Avarage relaxation times found in a 60/40 wt% mixture of PMMA (3 kg/mol) and M-THF. XPCS results show concentration fluctuations at q=0.003 Å^{-1} (open squares) and are compared to the molecular alpha relaxation optained from dielectric spectroscopy (full circles) and differential scanning calometry (diamonds).*

The analysis of the correlation functions measured was made by fitting a streched/compressed exponential Kohlrausch-Williams-Watts-function (KWW) to the data. For molecular glass forming systems usually streched exponentials are expected. In figures 1 and 2 the q-dependence of the avaraged relaxation times τ and the KWW-streching exponent β for different temperatures are shown. In our case the diffusive behaviour ($\tau \sim q^2$ and $\beta=1$) for low q and high temperatures changes continuously to non diffusive ($\tau \sim q$ and $\beta \neq 1$) for higher q and low temperatures. In recent literature this kind of behaviour is reported for a variety of soft matter systems out of thermal equilibrium, which undergo a jamming transition [Cip03, Fal06, Car08]. To our knowledge this has not yet been reported for molecular systems. In a jammed state the sample is not in thermal equilibrium. Since in our case the larger glass transition temperatur (two glass transitions are observed, cf. proposal) is 245 K, the results for T<250 K could also be interpreted in the way, that our sample fell out of equilibrium and underwent a jamming transition. The corresponding alpha-relaxation times obtained by dielectric relaxation are plotted in fig. 3, and the fitted Vogel-Fulcher curve cutts the concentration fluctuations at about the upper T_g. The two low temperature relaxation times of the concentration fluctuations clearly deviate from an Arrhenius-fit to the three high temperature points (indicated by the dashed line). Actually, this seems to be an indication of aging: the two points would relax to the dashed line for longer waiting times. This interesting observation has to be investigated in further experiments.

Also in the other samples (50% PMMA 3 kg/mol and 50% PMMA 15 kg/mol) concentration fluctuations could be detected, but the results are not completely unterstood and the analysis is still in progress. Another sample (50% Tristyrene in MTHF) did not exhibit sufficient contrast in electron density to get a signal, which can be correlated. In our proposal we also expressed the aim to make XPCS at scattering vectors corresponding to the wide angle regime of X-ray scattering. In a static scan we actually detected a structure peak with sufficient intensity at 1.28 Å^{-1}, but a multi speckle XPCS measurement with a CCD-detector has not been successful.

References

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