| | | |
|---|---|---|
| ESRF | **Experiment title:**<br>Concentration Fluctuations and Aging in Binary Glassformers | **Experiment number**:<br>SC-2818 |
| **Beamline**:<br>ID10A | **Date of experiment**:<br>from: 10/11/2009 to: 16/11/2008 | **Date of report**:<br>25/02/2010 |
| **Shifts:**<br>18 | **Local contact(s)**:<br>Dr Yuriy CHUSHKIN | *Received at ESRF:* |

**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

**Experimental Report:**

This project was a continuation of our experiment "SC-2557" in November 2008. Object of our investigations was to detect concentration fluctuations in a binary molecular glass former. The chosen sample system was a mixture of short chain Poly(Methyl-methyacrylate) (PMMA) and 40wt% Methyl-Tetrahydrofurane (MTHF), being characterized by a strong dynamic asymmetry, i.e. a large difference in the single component glass transitions (MTHF: $T_g$=91 K, PMMA: $T_g$=340 K). This property indeed induces the occurrence of two clearly separated glass transtitions in the mixture, although the sample is perfectly miscible in a broad temperature range and indications of demixing have not been observed at all. Furthermore, the PMMA-MTHF mixture is characterized by a strong contrast in electron density of the two components (MTHF: 288 El/nm$^3$, PMMA: 387 El/nm$^3$), which makes at particularly qualified for the analysis with X-rays.

X-ray Photon Correlation Spectroscopy (XPCS) was performed at beamline ID10A in SAXS geometry using a partially coherent 8 keV X-ray beam. For our samples two different PMMA polymers were used: one with 3100 g/mol and a large polydispersity index (PDI) of 2.9 and another nearly monidisperse one (PDI=1.05) with 4100 g/mol. 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].

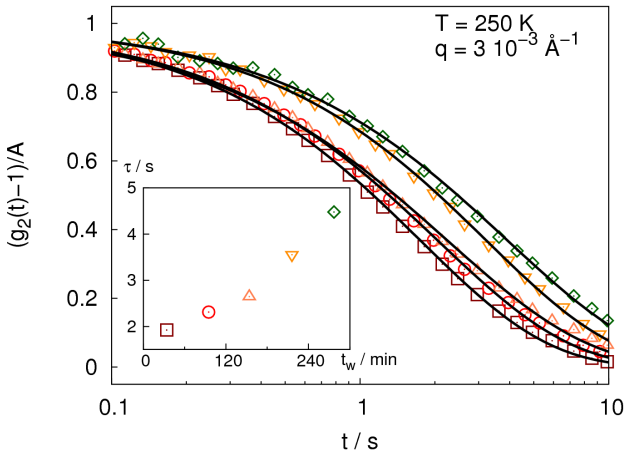


*Fig 1: Correlaton functions for 40% MTHF in 3100 g/mol PMMA at 250 K for different waiting times $t_w$. The inset shows the waiting time dependence of the average relaxation time.*

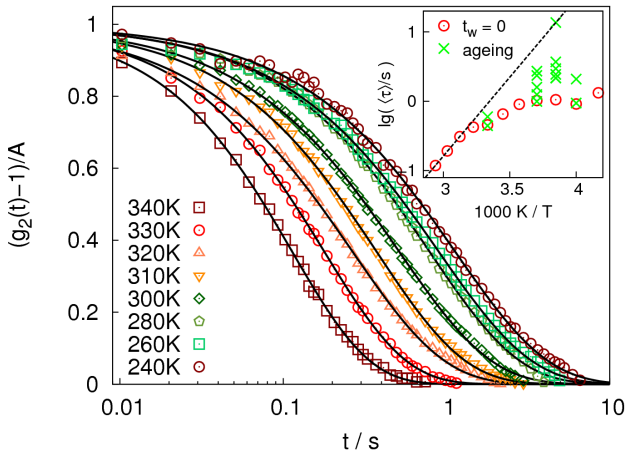


*Fig 2: Correlation functions for 40% MTHF in 4100 g/mol PMMA at $t_w$=0 for different temperatures. Inset: With increasing $t_w$ the relaxation times move towards the high temperature equilibrium line.*

The relaxation of concentration fluctuations has been measured at several temperatures far above, close to and even slightly below the upper glass transition of the mixtures. At high temperatures an Arrhenius-like temperature dependence of the average relaxation times was found, but when cooling down towards Tg deviations from this behaviour due to ageing occur. Already 40 K above $T_g$ the relaxation time starts to depend on the waiting time $t_w$, in the way that it becomes longer with increasing $t_w$. Fig. 1 shows the waiting time dependence of the measured correlation function and the corresponding relaxation times for 40% MTHF in 3100 g/mol PMMA slightly above $T_g$. One can see a monotonous slowing down of the relaxation by a factor of 2.5 in 280 minutes. In fig. 2 the temperature dependence of the relaxation for 40% MTHF in 4100 g/mol PMMA is shown. In the inset the relaxation times for $t_w$=0 as well as those for different waiting times are plotted vs. temperature. As a clear trend the relaxation times become slower with increasing waiting time and seem to move to the equilibrium Arrhenius-curve, which is defined by the high temperature measurements (dashed line in the inset of fig. 2). Nevertheless, the relaxation times at different $t_w$ also reflect the dynamical heterogeneity in our sample in the way, that deviations from the monotonous increase as shown in fig. 1 were observed. I.e., although the overall sample becomes slower, more mobile regions can move into the scattering volume and hence the relaxation does not change or even gets faster.

## References

[Duf02] E. M. Dufresne et al., *Phys. Rev. E* **65,** 061507 (2002)