ESRF	**Experiment title:** XPCS study of slow dynamics in a photosensitive poly-azo-acrylate glass-forming.	**Experiment number**: SC-1983
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Shifts: 20	**Local contact(s)**: Andrei Fluerasu	*Received at ESRF:*

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1. Introduction

In the experiment SC-1983 we pointed our attention to the density fluctuations dynamics of a polymeric system of the family of polyacrilates characterized by the insertion of a photoactive azobenzene unit in the side chains of each monomer.

The characterization of the microscopic and mesoscopic relaxation dynamics in this class of systems is doubly interesting both from the point of view of the dynamics itself and in the understanding of the mechanism underlying the photo-mechanical effects induced by the UV irradiation. We refer to the proposal for a more extensive discussion of our aim and to references [1,2] for more details about this class of systems and the effects induced by light while references in [3] can give an idea of the potential applications.

2.Experimental details

The experiment has been performed melting the polymer at around 100°C in order to shape it in a thin slice on the top of a copper holder. The slice has been pressed with a glass to obtain a flat surface 1x1 mm^2 with 0.2mm thikness. After removing the glass the slice has been placed with the surface parallel to the incoming X-rays with the beam incident 10-20 microns below the external surface. The holder has been placed inside a temperature controlled chamber. A fused silica optic fiber delivered the UV light directly to the top of the surface. A UV CW laser at 350 nm has been used with 5mW output from the fiber.

The multispeckles pattern from x-ray beam has been collected with the CCD detector.

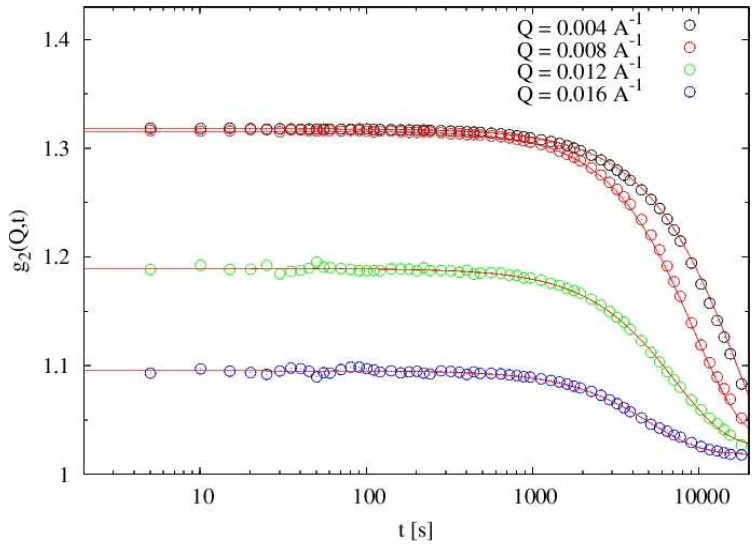

Fig 1: Correlation Functions for selected Q values at 27°C; the red line is the fit.

3.Data reduction and preliminary analysis

The normalized intensity correlation functions have been calculated from the CCD images using a "multitau" algorithm developed by Andrei Fluerasu and also observed as a function of the waiting time to exclude the possibility of a time-dependency of the results due to radiation damage or residual aging effects faster then expected.

The correlation functions have been fitted with a stretched exponential decay

$$g_2(q,t) = \beta(q)\exp\left(-(t/\tau)^{\gamma}\right)+1$$

In figure 1 the data and the fits are shown for the lowest temperature at some selected Q values. As it can be seen the fit quality is excellent. The relaxation time and exponent Q-dependence are shown in the two panels of figure 2: surprisingly the density fluctuations show a 'compressed' behavior of the relaxation and a Q^{-1}-dependency of the τ parameter. These results are in contrast with the general behavior expected for molecular glass-forming systems which use to exhibit stretched exponentials relaxations and the characteristic Q^{-2} dependency of the relaxation time typical of a diffusive behavior; in the specific case of this system a variety of techniques (including rheology, dielectric spectroscopy, depolarized Raman Spectroscopy, Quartz Crystal Microbalance) indicates a substantial agreement with this kind of glassy behavior characterized by stretched relaxations, albeit on much faster timescale than those reported in figure 2.

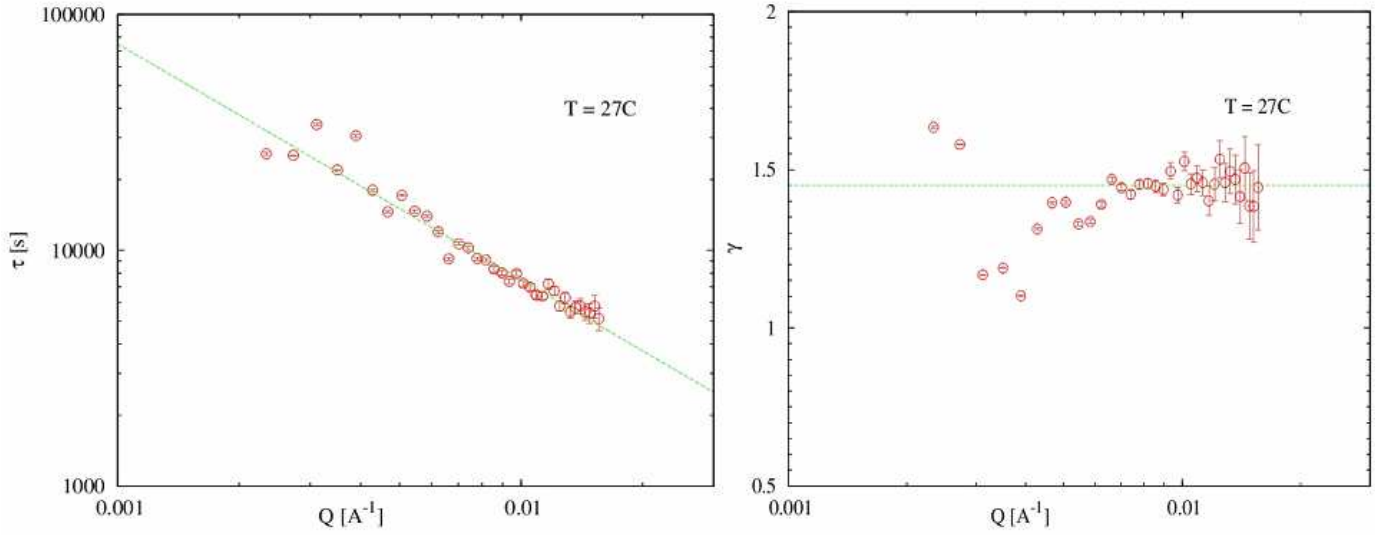

Fig 2: Q-dependency of the time scale and the exponent of the relaxation: the green line in the first panel shows a Q^{-1}- dependency

Nevertheless from a different perspective in the last years PCS [4,5] and XPCS[6] studies on a large variety of Soft Matter systems showed the same non-diffusive and 'compressed' behavior enhanced by figure 2, characterizing the final ultra-slow relaxation: Q^{-1} ballistic-like evolution and compression exponents around 1.5 have been found in these systems. The origin of this dynamics was firstly addressed [5] to continuous evolution of the strain fields generated by dipolar sources of internal stress as suggested by the model in [8]; nevertheless very recently [7] it has been pointed out for colloidal gels that the dynamics is not continuous but characterized by intermittent rearrangements as enhanced by the study of the fluctuations of the correlation function itself versus the waiting time: these kind of fluctuations are usually related (as suggested in glasses) to the presence of dynamical heterogeneities that introduce a correlation length so reducing the number of statistically independent regions. The Q-evolution of the amplitude of these fluctuations is also related to a crossover occurring at high Q in the average properties of the correlation funtions whose exponent comes back to the unity value. In ref. [7] it is suggested that the scale of the crossover is determined by the extension of the displacement of in a local rearrangement event
Despite peculiar of colloidal gels this scenario could have a kind of generality: up to now our data don't show real evidence of a crossover but could be extremely interesting to extend the investigation at higher Q values.

4. Photo-induced effects

After investigating the dynamics at two different temperatures we switched on the UV illumination at 32°C : also in this case the results was quite surprising as shown in figure 3. The expected fluidification induced by the UV light seems to affect the shape itself of the relaxation which recover the simple exponential decay law without any stretching or compression: as shown in the figure the exponent experiences a sudden jump from around 1.6 to the unity.

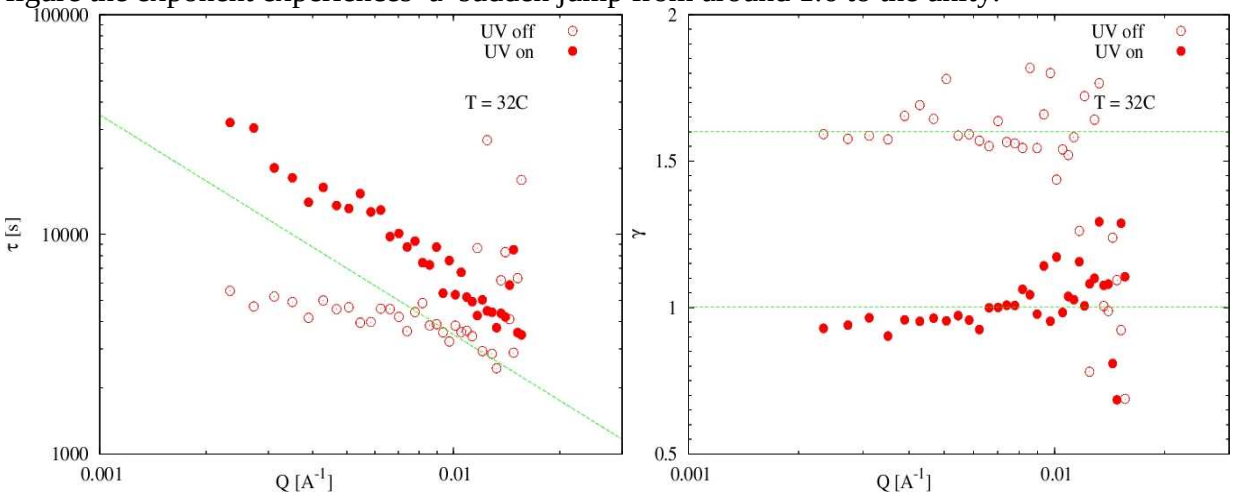

Fig 3: Q-dependency of the time scale and the exponent at 32°C measured with and without the UV illumination.

5.Conclusions

In conclusion from a preliminary analysis of the density correlation functions it has been shown that this class of azo-polymers shows on SAXS length scales the peculiar features found in many colloidal systems, meaning compressed exponential form of the decays and Q^{-1} -dependence of the relaxation time, rather than the usual stretched exponentials relaxation and the characteristic Q^{-2} dependency of the relaxation time, typical of a diffusive behavior and expected for molecular glass-forming systems.
Moreover the change in the shape of the relaxation induced by photoisomerization of the side chains is something peculiar, which warrants further investigation as a function of temperature and over a wider range in q-space.

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References

[1] G.S. Kumar and D.C. Neckers, Chem. Review, 89, 1915-1925 (1989),
A. Natansohn and P. Rochon, Chem. Review, 102, 4139 (2002).
[2] L. Cristofolini et al., J. Physics: Condensed Matter, 11 (1999) A355-362,
L. Cristofolini et al., Physical Review Letters 85, 4912 (2000).
L. Cristofolini et al., Philosophical Magazine B84, 1537, (2004).
[3] Z.F. Liu et al., Nature 34, 658 (1990),
T. Ikeda and O. Tsutsumi, Science 268, 1873 (1995).
P. Karageorgiev et al., Nature Materials 4, 699 (2005).
[4] R. Bandyopadhyay et al. Physical Review Letters, 93, 228302 (2003),
B. Chung et al. Physical Review Letters 96, 228301 (2006).
[5] L. Cippelletti et al. Physical Review Letters 84, 2275 (2000),
L. Cippelletti et al. Faraday Discussions, 123, 237 (2003).
[6] A. Robert et al. Europhysics Letters, 75, 764 (2006).
[7] L.Cippelletti et al. Europhysics Letters 76, 972 (2006).
[8] J.P. Bouchaud and E.Pitard, Eur. Phys. J. E, 6, 231 (2001).