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|  | <b>Experiment title:</b><br>XPCS study of the q-dependence of the slow dynamics in a photosensitive poly-azo-acrylate glass-former | <b>Experiment number:</b><br>SC-2556 |
| <b>Beamline:</b><br>ID10A  | <b>Date of experiment:</b><br>from: 05 February 2009 to: 10 February 2009  | <b>Date of report:</b><br>22.02.2009 |
| <b>Shifts:</b><br>15   | <b>Local contact(s):</b><br>Chiara Caronna   | <b>Received at ESRF:</b>             |
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The experiment was focused on the investigation of the dynamics of a photosensitive poly-azo-acrylate glass-former, the Poly[[4-pentiloxy-3'-methyl-4'-(6-acryloxyexyloxy)] azobenzene] henceforth named PA4. PA4 has glass transition temperature  $T_g = 20^\circ\text{C}$  and a nematic phase with clearing point  $T_{NI}=92^\circ\text{C}$ . The dynamics of this system is strongly dependent on the isomerization of its side chain, since illumination with UV light ( $\lambda = 350\text{ nm}$ ) induces fluidification because of the azobenzene photoisomerization from trans to cis isomer, with variations of both sample's viscosity and density. Instead, illumination with visible light ( $\lambda = 480\text{ nm}$ ) induces continuously switching between the cis and trans isomers of the azobenzene group, leading to a variation in viscosity only [1,2].

By means of XPCS we measured the q-dependence of the relaxation time  $\tau$  under different illumination conditions. The samples consisted of Langmuir-Schaefer PA4 multilayers on silicon, 150nm thick as measured by ellipsometry. All the experiments were performed with incident energy 8063eV, with the collimation pinhole set to 10 microns, at an incidence angle below the critical angle for the penetration of the beam into Si, thus minimizing the photo-electrons that are one of the main reasons of radiation damage for our sample. Illumination with UV and visible light was provided by two air-cooled LED arrays placed around 5 cm away from the sample. Helium was fluxed into the sample chamber in order to keep a controlled atmosphere and minimize radiation damage.

We experienced different experimental geometries: to probe surface dynamics we worked below the critical angle for PA4/air interface. The capillary waves correlation functions we measured ( $q < 10^{-3}\text{ \AA}^{-1}$ ) are characterized by relaxation times longer than  $10^4$  seconds, therefore inaccessible in a reasonable experimental time (figure 1).

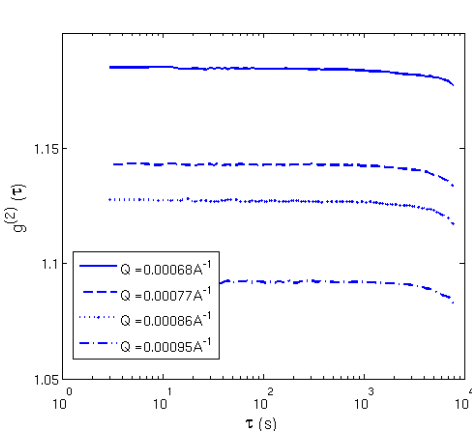


Figure 1: Correlation functions relative to surface dynamics (capillary waves). In the q-region investigated ( $q < 0.001\text{ \AA}^{-1}$ ), relaxation times are greater than  $10^4\text{ s}$ , thus impossible to be measured.

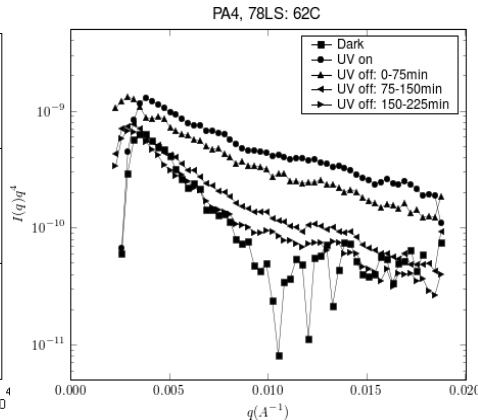


Figure 2: Porod plot of  $I(q)$ , at different illumination conditions. The change induced by UV light is completely thermally reversible.

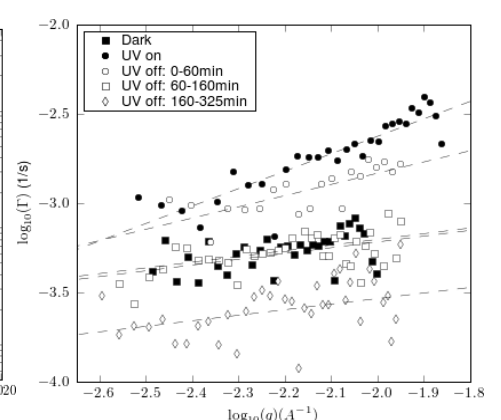


Figure 3:  $\Gamma(q)$  measured at  $62^\circ\text{C}$ , at different illumination conditions in the GISAX geometry. The change induced by UV light is thermally reversible.

Looking for faster dynamics we reverted to the GISAXS geometry. In figure 2, the Porod plot of the scattered intensity  $I(q)$  is reported. Exposing the polymer to UV light causes an increase in  $I(q)$ : the scattered intensity relaxes back [3] to the value previously measured in complete obscurity when light is turned off. Correlation functions were fitted with a stretched exponential curve, obtaining the  $q$ -dependence of both the compression exponent  $\gamma$  and the exponent  $\Gamma=1/\tau=Dq^n$  as functions of temperature and illumination condition. Figures 3 and 4 report data at 62°C: for PA4 in dark we observe  $\Gamma \propto q^{0.4}$ , a behaviour already observed in aged glasses [4] and adhesive colloids [5,6], while under UV illumination the dynamics reverts to the “normal” behaviour  $\Gamma \propto q^1$ , which is common in polymeric systems and colloidal gels [5,7]. This transformation is reversible, as our back-to-equilibrium relaxation experiment shows (fig 3).

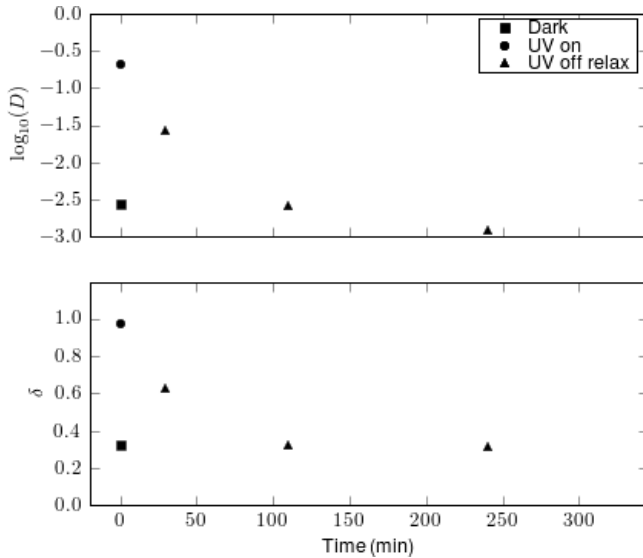


Figure 4: Parameters obtained fitting data of figure 3 with  $\Gamma=1/\tau=Dq^n$ , at 62°C: under UV light, PA4 behaves like a polymer with  $n=1$ , while in dark we observe a sublinear  $q$ -dependence.

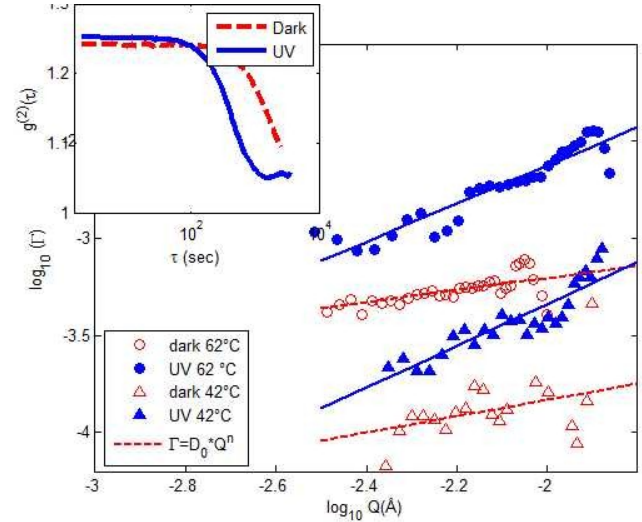


Figure 5: Comparison of data measured at 62°C and 42°C, in dark (red symbols) and under UV light (blue symbols). As the temperature is varied, the exponent  $n$  (the slope of the lines) remains constant, while diffusion becomes faster at higher temperature.

We also performed a preliminary study as a function of the temperature: the data are shown in Fig 5, in dark and under UV illumination, at 42°C and 62°C: data analysis is underway, however we can notice that the exponent  $n$  (the slope of the lines) seems to be independent of the temperature but clearly affected by the UV illumination, while the proportionality constant  $D$ , a sort of generalized “diffusion coefficient”, is lower at lower temperature, in agreement with the expected global slowing down of the dynamics.

We also performed experiments under visible light illumination, at a wavelength which is known to reversibly cycle the azo-moieties between their trans and cis conformations. The experiment proved to be problematic, possibly due to some radiation damage, however a more detailed data analysis is under way.

The very long relaxation times observed for PA4 require an adequate number of experimental shifts in order to be completely measured. Unfortunately, the first day of measurements was lost due to a wrong alignment of the electron beam after the MTD. We anticipate that further investigation should be conducted at higher  $q$ , where dynamics is faster, in particular around the structure factor peak at  $1.5\text{\AA}$ , even if in this case some DeGennes narrowing is to be expected.

## References

- [1] L. Cristofolini et al., J. Physics: Condensed Matter, 11 (1999) A355-362.  
L. Cristofolini et al., Philosophical Magazine B84, 1537, (2004).
- [2] L. Cristofolini et al., Physical Review Letters 85, 4912 (2000).
- [3] L. Cristofolini et al. Phys. Rev. E, 64 061803 (2001)  
P. Camorani et al. Phys. Rev. E 73, 011703 (2006)
- [4] Fluerasu et al, Phys. Rev. E 76, 010401(R) (2007)
- [5] Cipelletti and Ramos, Current Opinion in Colloid & Interface Science Vol.7, Issues 3-4 (2002) 228-234
- [6] Solomon and Varadan, Phys. Rev. E 63 05140 (2001)
- [7] Duri and Cipelletti, Europhys. Lett. 76, 972 (2006)