	Experiment title: Illumination and temperature dependence of the slow dynamics of a film of photosensitive azopolymer by surface XPCS.	**Experiment number**: SC-2820
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By this experiment we integrated our preliminary investigation (SC2556, Feb 2009) of the dynamics of a photosensitive poly-azo-acrylate glass-former, namely poly[[4-pentiloxy-3'-methyl-4'-(6-acryloxyexyloxy)] azobenzene] henceforth called PA4, which has bulk T_g = 20°C and a nematic phase with clearing point T_{NI}=92°C [1]. The dynamics of this system is strongly dependent on the isomerisation of its side chain, which can be driven by the light: UV induces fluidification while visible light (λ = 480 nm) induces continuously switching between the cis and trans isomers of the azobenzene group, leading to a variation in viscosity [2,3].

Based on our previous experience we focused on a particular geometry optimized for both the efficiency of the photoperturbation and the XPCS data collection: we used 8063eV x-ray radiation, a 10x10 μm pinhole and guard slits to block interference fringes positioned as close as possible to the sample position. The polymer was deposited as a a 150nm thick Langmuir Schaeffer film on silicon substrate, which was placed at incidence angle of 0.15° in the incoming x-ray beam, well below the critical angle for total reflection from silicon/air interface (α_c=0.22°), but large enough to have penetration of the x-ray beam in the depth of the polymer (thus avoiding the pure surface scattering geometry sensitive to capillary waves, which are known to be slower than the bulk dynamics inside the polymer). Scattered intensity was collected by the medipix detector and integrated in the "out of plane" perpendicular direction, thus focusing in the in-plane dynamics inside the film and excluding any contribution from the surface. We focused on a few selected temperatures well above T_g: 42°, 62°, 72° and 85°C. Attempts to investigate higher temperatures proved unsuccessful because the polymeric molecular multilayer starts to retract and form droplets: the so called "dewetting" phenomenon. We explored different illumination conditions (dark, UV and visible light) with samples either of pure polymer, or of gold nanoparticles (GNP) of radius 7.9nm diluted in the polymeric film, which are expected to act as tracers of the polymer dynamics. In the following we report firstly on the pure polymer, then on the GNP system.

Typical temporal intensity correlation functions, together with their best fit by a KWW stretched/compressed exponential form $g^{(2)}(q, t)=A(q)+\beta(q)*\exp(-2(t/\tau)^\gamma)$ are shown in Figure 1 for PA4 under UV illumination at 62°C.
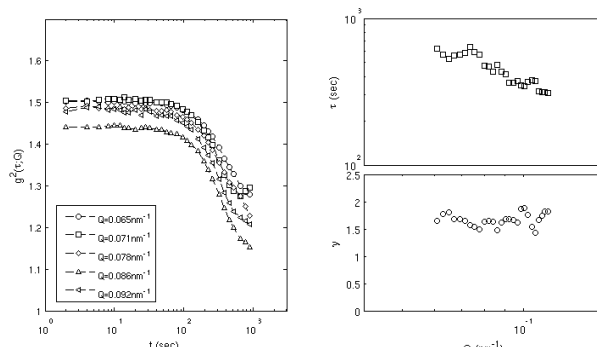

Figure 1 *left: correlation functions for PA4 at 62°C under UV,* **right**: *best fitting values for correlation time τ and exponent γ*

For the data analysis we proceeded as follows: we first filtered the data by excluding some of the individual detectors of the Medipix which had an average signal or a standard deviation significantly different from the "ensemble average" computed over all the individual detectors corresponding to an individual q. We then calculated q-averaged correlation functions and fitted each correlation function with all the parameters left free to vary, finding the relaxation rates τ shown in figure 2 as a function of the exchanged momentum q for the different temperatures and illumination conditions. In the subsequent analysis we heuristically rejected 10% of the data corresponding to the worst fits as measured by the χ^2 test.
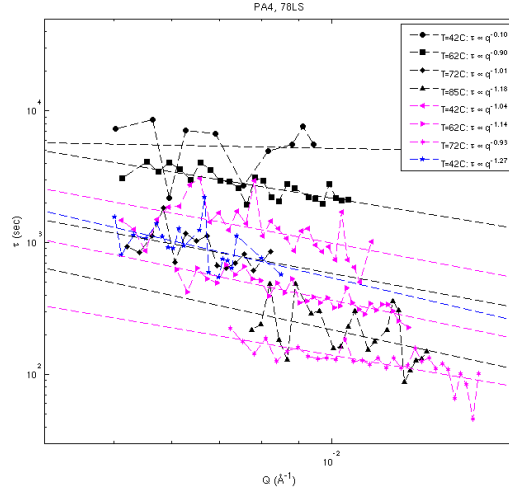

Figure 2: *Relaxation times τ as a function of the momentum q, for PA4 at the different temperatures and illumination conditions.*

In this way we could fit the algebraic q-dependence of the relaxation time τ, as shown by the dashed lines in figure 2. The power exponent n is on average 1 for all the temperatures both in dark and under UV, as shown in figure 3 (left), the KWW compression exponent γ shows no q dependence within the experimental uncertainty (see bottom right panel of figure 1) but it depends from the temperature, ranging from compressed (γ=1.5) at the lower temperatures to a value closer to 1 at the highest temperatures (figure 3, right panel). At the same time the contrast β and the baseline A varied from one cf to another without any apparent regularity but with β staying around 0.3 and the baseline A around 1 as expected.

A similar $\tau \sim q^{-1}$ scaling and 'compressed exponential', i.e. γ>1, has been measured by XPCS in a wide variety of materials [4], including both attractive systems (fractal colloidal gels [5]) and repulsive systems (compact arrangements of soft elastic spheres [6] or of emulsion droplets [7], and Laponite [8]). This scaling suggests that the slow dynamics be due to a 'ballistic' motion of the particles, in the sense that the average particle displacement grows linearly with time, while models based on cage-escape processes must be ruled out. Therefore it has been proposed [5-7] that the dynamics could be due to randomly distributed internal stress sources acting on the sample, whose response is that of an elastic solid. The unusual dynamics reported above may therefore be due to a series of discrete rearrangement events as discussed in a number of publications [4]. The mechanism underlying this is at present unclear: while for colloids one can postulate intermittent rearrangement of larger or smaller volumes whose size can be estimated by some "crossover" q at which the compression coefficient varies from 1 to 1.5 [4], the situation is much less clear for polymeric systems, for which some predictions have been formulated based on a model of an elastic medium with random dipolar interactions by Bouchaud and Pitard [9] in which a crossover from γ=3/2 to 5/4 is predicted when some characteristic time scale τ_q. To the best of our knowledge, such crossover has not been experimentally verified yet. If we assume τ_q to be temperature dependent and shorten upon heating, we can then interpret our experimental result as an *indirect* evidence for such crossover. Our data from PA4 are therefore at least consistent with the detailed predictions of ref [9].
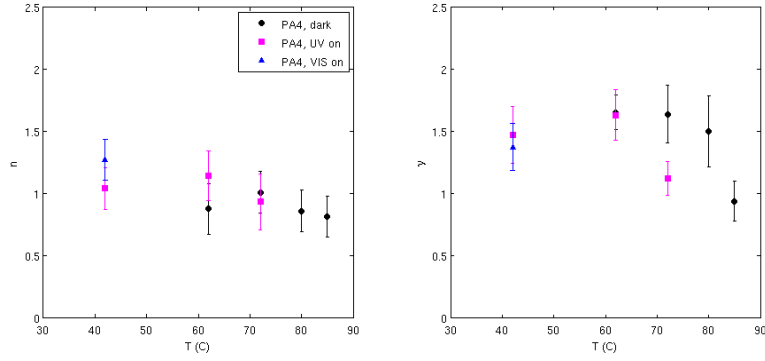
Figure 3: *Temperature evolution of the exponents n and γ*

It is also interesting to compare the relaxation times at the same temperature in dark τ_{DK} and under UV illumination τ_{UV}: the red points in figure 4 are the ratio τ_{UV}/τ_{DK} which is found to be fairly independent from T, showing photoinduced acceleration of the dynamics by a factor of 10. This is in qualitative agreement with out Interfacial Shear Rheometry (ISR) measurements on a Langmuir film, in which we found a reduction of the dissipative (imaginary) part of the shear modulus G" by a factor 700 (figure 4, right panel). A direct comparison of ISR and XPCS results is made difficult by the above mentioned characteristic of XPCS not observing Brownian diffusion but some other kind of relaxation, which is however surely viscosity-related. We also performed a measurement under visible light which is known from our ISR measurements to increase the polymer's shear modulus at least on the macroscopic scale. Surprisingly we found a *decrease* of the correlation time comparable or even larger than that obtained by UV illumination. We speculate that this can be explained by taking into account the different length scales involved in the experiments: in XPCS we measure dynamics on the local scale, which is surely faster due to the isomerisation cycles induced by the VIS illumination (both *cis* and *trans* isomers absorb light with approximately the same efficiency at this wavelength). At the same time this cyclic isomerisation increases the shear modulus of the film measured over long distances (hence that measured by ISR) because reduces defects and borders of grain, in a similar manner as annealing would do.
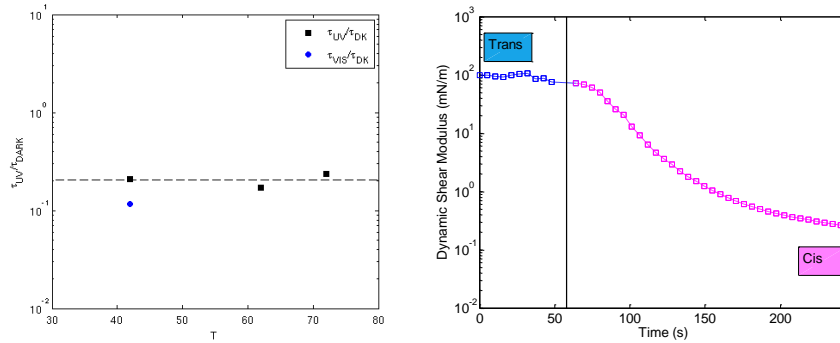

Figure 4: left: *relaxation times under UV and under visible illumination normalized to the corresponding value in dark (τ_{UV}/τ_{DK}, τ_{vis}/τ_{DK})* **right**: *evolution of the dissipative part of the shear modulus G" in a single molecular layer in dark and under UV measured by Interfacial Shear Rheometry.*

We also analyzed the temperature dependence of the relaxation times as shown in the Arrhenius plot of figure 5. We compare our data against the Vogel Fulcher Tammann law for PA4 (T_0 =243K, activation temperature T_a=1270K) found by EPR [2] and confirmed by depolarized micro Raman and Quartz Crystal Microbalance [3]. Inspection of Fig 5 shows that the same VFT law is obeyed by our relaxation data excluding the lowest studied temperature (42°C, on the right in the Arrhenius plot), which provides us a nice confirmation of the quality of our data and at the same time gives us a strong warning that the slow dynamics expected close to Tg could be unobservable because of some other events- such as beam or sample instabilities- take place on a relatively shorter time scale.
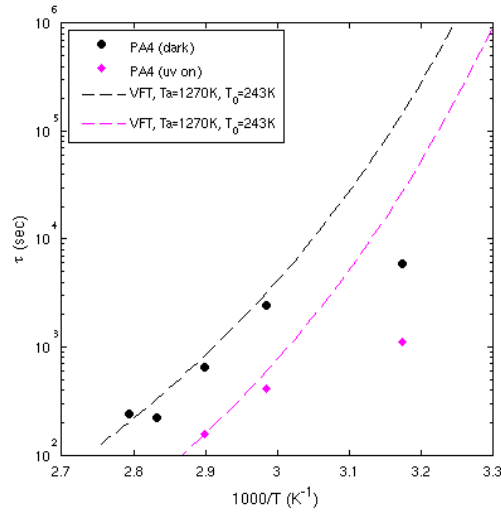
Figure 5: *Arrhenius plot of tau in dark, UV and vis illumination, all at the same value of Q=0.09nm^{-1} together with the well characterized VFT law for PA4.*

We also extended our investigation to the dynamics of gold nanoparticles (GNP) embedded in the layer, with the idea that they should act as tracers for the dynamics inside the polymer [11] while providing good contrast to the X-rays. GNP have been synthesized according to [12], have been characterized by SAXS at our home laboratory: they have radius R=7.8nm with negligible dispersion. We investigated different dilutions, from 0.05% to 1% in weight. In figure 6 we report typical relaxation times obtained at the different illumination conditions.
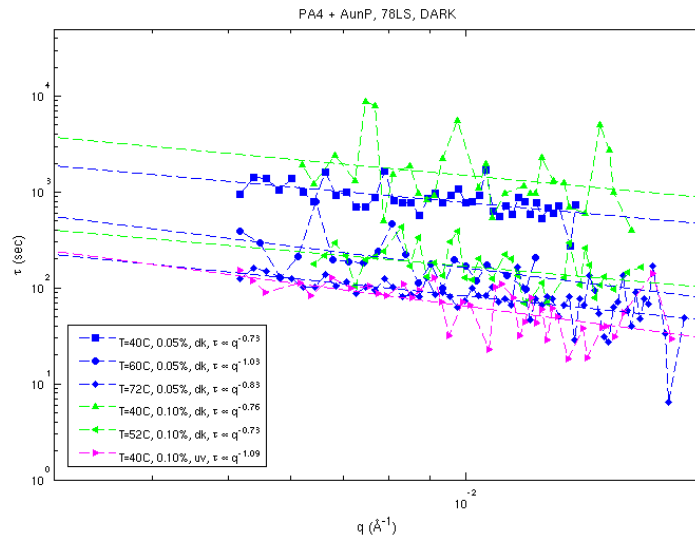

Figure 6: *Relaxation time as a function of the momentum q, for GNP in PA4.*

As shown in figure 7, in dark we find that the KWW compression exponent γ is 1.5 within the error for all the concentrations studied, and the relaxation time follows an inverse linear dependence from q in close resemblance with the case of pure PA4, and also with what reported in the literature [11,13] for a similar system comprising of GNP diluted in polystyrene in the limit of small momentum q and low temperature. This scenario has been described as "superdiffusive" and is expected to evolve to classical Brownian diffusion at higher temperatures [11].
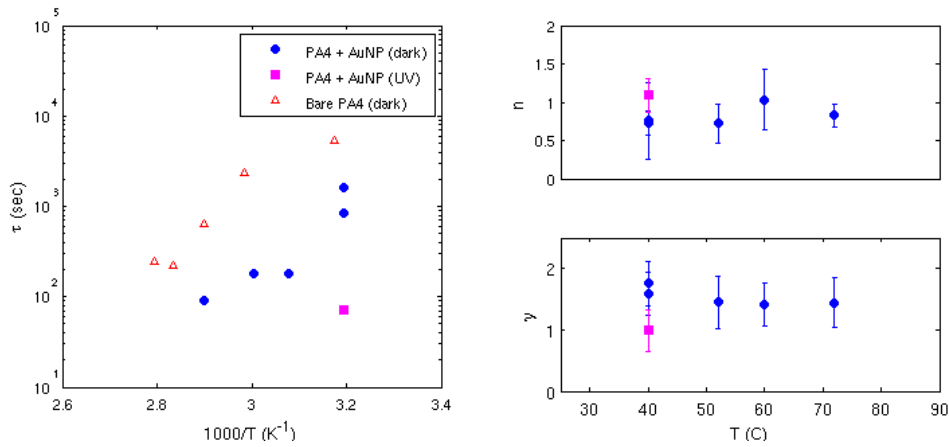
Figure 7: left *Arrhenius plot for the relaxation time of GNP in PA4 film.* **Right:** *temperature dependence of the exponents n and γ*

We also measured the same system under UV illumination (pink points in figure 7) finding *i)* a marked decrease of the correlation time by a factor 30 (therefore larger than in pure PA4, as shown in figure 4) and *ii)* a change in the shape of the relaxation, with the KWW exponent γ decreasing to 1 (pure exponential relaxation) as predicted by simple diffusion, however at the same time the q-dependence is still superdiffusive. We believe that this point deserves further investigation, however we are tempted to describe this scenario as the crossover from superdiffusive to Brownian in agreement with the literature [11].

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