

Slow dynamics in an azopolymer molecular layer studied by x-ray photon correlation spectroscopyDavide Orsi,¹ Luigi Cristofolini,¹ Marco P. Fontana,¹ Emanuele Pontecorvo,² Chiara Caronna,³ Andrei Fluerașu,⁴ Federico Zontone,⁵ and Anders Madsen⁵¹*Physics Department, University of Parma, Viale Usberti 7/A, Parma 43100, Italy*²*Physics Department, University "La Sapienza", I-00185 Roma, Italy*³*SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, USA*⁴*Brookhaven National Laboratory, NSLS-II, Upton, New York 11973, USA*⁵*European Synchrotron Radiation Facility (ESRF), 6 rue J. Horowitz, 38043 Grenoble, France*

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We report the results of x-ray photon correlation spectroscopy (XPCS) experiments on multilayers of a photosensitive azo-polymer which can be softened by photoisomerization. Time correlation functions have been measured at different temperatures and momentum transfers (q) and under different illumination conditions (dark, UV or visible). The correlation functions are well described by the Kohlrausch-Williams-Watts (KWW) form with relaxation times that are proportional to q^{-1} . The characteristic relaxation times follow the same Vogel-Fulcher-Tammann law describing the bulk viscosity of this polymer. The out-of-equilibrium relaxation dynamics following a UV photoperturbation are accelerated, which is in agreement with a fluidification effect previously measured by rheology. The transient dynamics are characterized by two times correlation function, and dynamical heterogeneity is evidenced by calculating the variance χ of the degree of correlation as a function of ageing time. A clear peak in χ appears at a well defined time τ_C which scales with q^{-1} and with the ageing time, in a similar fashion as previously reported in colloidal suspensions [O. Dauchot *et al.*, *Phys. Rev. Lett.* **95**, 265701 (2005)]. From an accurate analysis of the correlation functions we could demonstrate a temperature and light dependent cross-over from compressed KWW to simple exponential behavior.

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I. INTRODUCTION

The use of photoinduced isomerization to produce actuator materials was proposed by de Gennes [1] long ago and since then a wide literature flourished; however, very few real applications emerged, mainly because of an insufficient understanding of the fundamental properties of this class of materials. In particular, a great deal of work has been focused on side-chain liquid crystalline polymers with an azobenzene moiety attached to the main chain via a flexible molecular spacer [2–5] also because of potential applications for information storage [6–10].

Photoinduced effects on the mechanical properties of polymers, and the related possibility of controlling them by appropriate illumination, are poorly understood despite their interest for a number of applications, including drug delivery, specialized fabrics, light-activated damping mechanisms, actuable armours, and related applications in fields such as robotics and sensors. There is general consensus on the fact that photoinduced isomerization of azobenzene polymers results in softening or mechanical fluidification, even if a detailed understanding of the mechanism by which this happens is lacking; it is one of the purposes of the present study to understand this. An irreversible change by more than four orders of magnitude in the viscosity was recently found by Ketner *et al.* [11], while smaller but reversible changes have been reported in azobenzene siloxanes [12] and azobenzene elastomers [13]. The same effects have also been confirmed at the level of Langmuir monolayers [14].

In the present work we focus on a particular polymer, poly[[4-pentiloxy-3'-methyl-4'-(6-acryloxyoxyloxy)] azobenzene] henceforth called PA4, which has a bulk glassy

phase with $T_g=20$ °C and a nematic phase with clearing point $T_{NI}=92$ °C [15,16]. In the past we applied the Langmuir-Blodgett (LB) technique [17] to obtain monolayers and multilayers of this polymer, and studied the effects of thickness on the structure and dynamics [18]. In a following experiment [19] the effect of temperature and photoperturbation were investigated on thick films and on superstructures formed by the intercalation of fatty acids (Ba Behenate) and azopolymer molecular layers. This work demonstrated the possibility of generating nanostructured glasses with a controlled size and morphology.

In the present work we take advantage of this experience to study slow dynamics inside a photosensitive azopolymer as a function of temperature and photoperturbation, exploiting the spatial resolution in x-ray photon correlation spectroscopy (XPCS) experiments [20]. The main advantage of using x-rays instead of direct methods (e.g., scanning probe microscopy) is that it provides statistical information averaged over the whole sample as a function of the momentum transfer q . This is essential for the analysis of dynamical heterogeneity and of nonequilibrium and aging effects in the observed dynamics. Indeed, dynamical heterogeneities have been observed in recent molecular dynamics (MD) simulations [21] with a pronounced effect of photoisomerization on the nonequilibrium dynamics. On the experimental side, time-resolved XPCS, i.e., the so-called two times analysis [22,23] offers a truly unique way of directly accessing q -resolved dynamical heterogeneities [24], and was used here, as described further below.

Out of equilibrium systems often display very complex dynamics that is far from being described by simple Brownian motion. Examples include clay suspensions [25,26] colloidal gels [24,27–29] or concentrated emulsions [30]. In all

these systems, the bulk dynamic structure factor is well described by a peculiar universal form—compressed exponentials—and shows a complex time dependence (i.e. “aging”).

In recent papers [31,32] XPCS was used to measure the dynamic structure factor of gold nanoparticles moving on the surface of thin polymer films. Above the glass transition of the polymer a stretched or compressed KWW behavior of the correlation functions was observed depending on the thermal history of the sample. The relaxation rates appeared to scale linearly with q , ruling out a simple Brownian diffusive motion. Excluding overdamped capillary waves as the origin of the linear behavior, the authors drew resemblance with aging bulk soft matter systems governed by a power law distribution of particle velocities due to ballistic motion. However, the sample was prepared by evaporation of gold on the polystyrene film: in this way the film is driven out of equilibrium and its dynamics could be altered by this procedure. Therefore further investigations are required to clarify the role of aging.

II. EXPERIMENT

The XPCS experiments were performed using partially coherent x rays at the ID10A beamline (Troika) of the European Synchrotron Radiation Facility. A single bounce Si(111) crystal monochromator was used to select 8.06 keV x rays, having a relative bandwidth $\Delta\lambda/\lambda \approx 10^{-4}$. A Si mirror downstream of the monochromator was used to suppress higher energy x rays from the monochromator. A transversely coherent beam was defined by slit blades with highly polished cylindrical edges. The slit size was $10 \times 10 \mu\text{m}^2$. A set of guard slits was placed just upstream of the sample to block the parasitic scattering due to diffraction from the beam-defining slit. The scattering from the sample was recorded by the Maxipix detector [33] which consists of 256×256 pixels each of $55 \times 55 \mu\text{m}^2$ area, located 2.2 m downstream of the sample. In this way q ranging from 0.005 to 0.2 nm^{-1} was accessible. Focusing on the slow dynamics, we collected speckle patterns every 1–10 s, being limited on the long time side only by the overall instrumental stability yielding an upper limit of a few hours in the accessible timescales.

Based on previous experience we employed a particular experimental geometry, sketched in Fig. 1, designed to optimize both the efficiency of the photoperturbation and the XPCS data collection as explained in the following. The polymer sample was a 75 molecular layer thick multilayer prepared on a silicon substrate using Langmuir Schaeffer deposition. It was extensively characterized by null-ellipsometry, AFM, and SEM microscopy. We found the thickness of each individual monolayer to be about 2 nm (which gives a total thickness of 150 nm for a sample made of 75 layers) and a typical surface roughness of 1 nm, in excellent agreement with the typical values previously reported for films of this polymer [18,19]. The sample was then oriented to have the x-ray beam impinging at a grazing angle of 0.15° , i.e., above the critical angle for total external reflection from the polymer-air interface but well below the

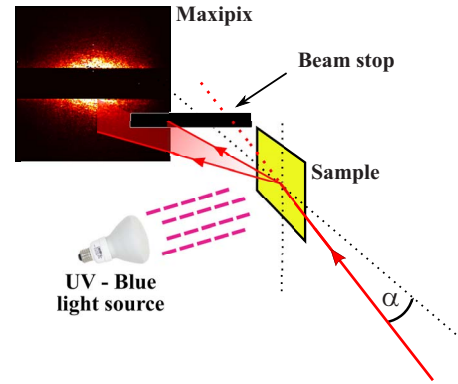


FIG. 1. (Color online) Experimental setup. The incoming and reflected x-ray beams are indicated by continuous (red online) lines. The sample is aligned at an angle of $\alpha=0.15^\circ$ with respect to the incident beam. UV/blue light sources provide photoperturbation as needed. The beam stop blocks the specular reflected x-ray beam before the Maxipix detector, which collects the diffuse scattering.

critical angle for total reflection from the silicon substrate ($\alpha_c^{\text{Si}}=0.22^\circ$). This allows measurements of small angle scattering from the polymer around the specular reflection, and at the same time it minimizes radiation damage to the polymer sample caused by x-ray induced photoelectrons emitted by the Si substrate. It has to be emphasized that the bulk of the polymer is probed—and not its surface, at difference from other experiments as, e.g., [32], where the dynamics investigated arose from surface capillary waves. Therefore in the present geometry the transfer momentum q is calculated from the radial distance between each pixel and the specular reflected beam, as in a transmission geometry SAXS experiment. The scattered intensity follows loosely the Porod law ($I \approx q^{-4}$) with a maximum intensity of a few hundreds of counts per second in the smallest q region. Distribution of density inhomogeneities inside the polymer is deemed responsible for the scattering.

Photoperturbation was provided by two different light sources placed in front of the sample. The sample thickness was calibrated to ensure a rather homogeneous light power density. In total we explored three different illumination conditions: dark, UV ($\lambda \sim 360 \text{ nm}$) and visible light ($\lambda \sim 480 \text{ nm}$). UV illumination is expected to alter the *cis-trans* equilibrium in favor of the *cis* configuration, whereas at 480 nm both *cis* and *trans* configurations are pumped with roughly the same efficiency, yielding a continuous cycling of the azobenzene molecules between the two states. We focused on a few selected temperatures well above T_g , between 42 and 85°C . Attempts to investigate higher temperatures proved unsuccessful because the polymeric molecular multilayer starts dewetting from the substrate and forms droplets

For the data analysis we proceeded as follows: first, individual pixels of the Maxipix detector were grouped in 15–25 q -bins according to the values of their in-plane momentum transfer q . Subsequently, every q -bin was filtered by excluding those pixels with average signals or standard deviations significantly different from the average values. The intensity autocorrelation functions $g^{(2)}(q, t)$ defined as

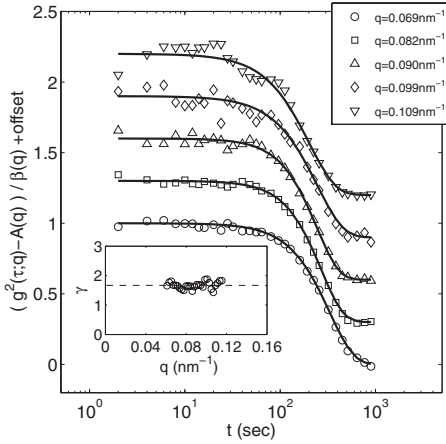


FIG. 2. Normalized correlation functions for PA4 at 72 °C under UV illumination, together with the best KWW fits (solid lines). Data are offset in steps of 0.3 for clarity. Inset: best fitting values for the compression exponent γ .

$$g^{(2)}(q, t) = \frac{\langle I(q, t_0) \cdot I(q, t_0 + t) \rangle}{\langle I(q) \rangle^2}, \quad (1)$$

were then calculated. Here $I(q, t_0)$ is the intensity measured at time t_0 and wave vector q and the average $\langle \dots \rangle$ is performed over all the pixels in the q -bin and, for stationary dynamics, also over all initial times t_0 .

The correlation functions were then fitted by a Kohlrausch-Williams-Watts (KWW) modified exponential form

$$g^{(2)}(q, t) = A + \beta \cdot e^{-2[t/\tau(q)]^{\gamma(q)}}, \quad (2)$$

where A is the baseline, typically equal to unity, β is the contrast of the correlation function which in this geometry is around 0.3. $\tau(q)$ is the q -dependent characteristic relaxation time; it usually follows a power law with exponent n : $\tau \propto q^n$. Finally, $\gamma(q)$ is the KWW exponent, also dependent on q .

III. RESULTS AND DISCUSSION

Equilibrium dynamics. We first focus on the dynamics in the two different equilibrium configurations of the material either in dark or under UV illumination limiting the investigations to the long time stationary regimes. The out-of-equilibrium dynamics shall be discussed in the next section.

The first effect of UV photoperturbation is to alter the *cis/trans* isomer ratio. This happens typically on a subsecond timescale [6]. A slower mechanical expansion of the film takes place on a time scale up to about 100 s at 60 °C [34]. All the results reported in this section were obtained long time after the application of photoperturbation. Typical correlation functions, together with their best fits are shown in Fig. 2 for PA4 at 72 °C after it has reached its equilibrium state under UV illumination.

Each correlation function was fitted with the KWW form with all parameters left free to vary. In the subsequent analysis we heuristically rejected about 10% of the data corre-

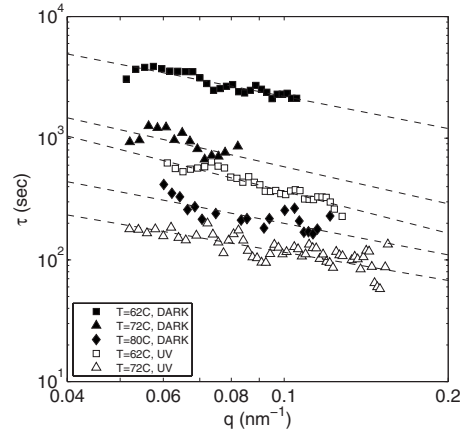


FIG. 3. Relaxation times (τ) in the equilibrium state as a function of q at the different temperatures and illumination conditions indicated in the caption.

sponding to the worst fits as measured by the χ^2 test. The extracted relaxation times τ are shown in Fig. 3 as a function of q for different temperatures and illumination conditions. Power law fits are shown by the dashed lines in Fig. 3 which clearly shows a speeding-up of the dynamics upon UV illumination. As shown in Fig. 4 (top left) the exponent n is on the average -1 for all temperatures both in dark and under UV illumination. The KWW exponent γ shows no significant q dependence (see inset of Fig. 2 for an example) but it depends on the temperature, with a correlation function de-

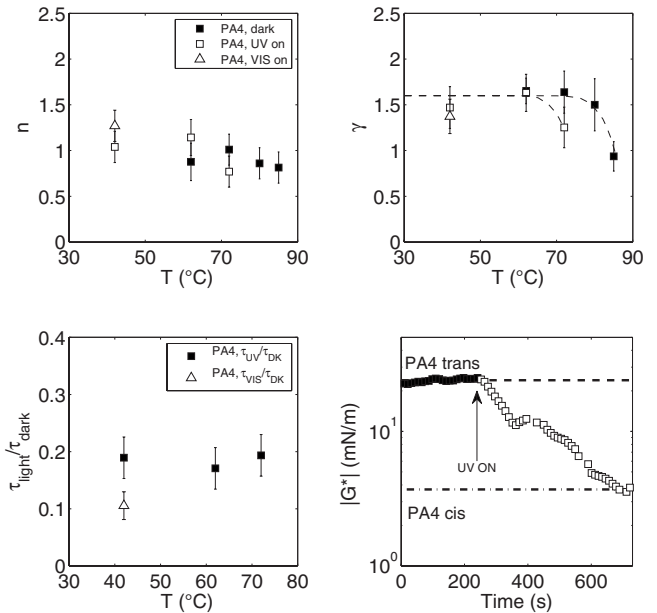


FIG. 4. Top left: temperature evolution of the exponent n at different illumination conditions; top right same for γ averaged over the investigated q range; the dashed lines are guides to the eyes. bottom left: XPCS measurement of the photoinduced acceleration of dynamics, quantified by the ratio of relaxation times (τ_{UV}/τ_{DK} , τ_{vis}/τ_{DK}) bottom right: interfacial shear rheometry measurement of photoinduced fluidification: evolution of the shear modulus $|G^*|$ in a Langmuir molecular layer of PA4 in dark and under UV light.

caying faster than exponentially ($\gamma=1.5$, compressed exponential behavior) at the lower temperatures and a value closer to $\gamma=1$ (simple exponential) at the highest temperatures (see Fig. 4, top right panel). At the same time the contrast β and the baseline $A(q)$ varied slightly from one correlation function to another without any apparent regularity but with β always close to 0.3 and $A(q)$ around 1, as expected.

A similar $\tau \sim q^{-1}$ scaling and compressed exponentials, i.e., $\gamma > 1$, has been measured by XPCS in a wide variety of materials [35], including both attractive (fractal colloidal gels [27]) and repulsive (compact arrangements of soft elastic spheres [36], of emulsion droplets [37], and Laponite [25]) systems. This scaling suggests that the slow dynamics is of ballistic nature, in the sense that the average mean-square displacement grows as time squared. It has been proposed [27,36,37] that the dynamics could be due to randomly distributed stress sources within the sample, whose response mimics that of an elastic solid. The dynamics may therefore be caused by a series of discrete rearrangement events as discussed in a number of publications [35]. The mechanism underlying this is at present unclear: for colloids and related systems, following Cipelletti, 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 [35]; however, the situation is much less clear for polymeric systems. Here predictions have been formulated based on a model by Bouchaud and Pitard concerning an elastic medium with random dipolar interactions [38] with a crossover from $\gamma=3/2$ to $5/4$ at some characteristic time scale τ_q . We assume τ_q to be temperature dependent and to decrease upon heating following the temperature dependence of the viscosity. We can then interpret our experimental result of the decrease of γ upon heating (above 80 °C for *trans* PA4, dark, and above 65 °C for *cis* PA4, UV) as support for such a crossover.

Moreover, the different crossover temperatures for dark and UV illuminated PA4 (approximately 15 °C difference), clearly show that UV photoperturbation accelerates the molecular dynamics, as demonstrated by the data in the bottom left panel of Fig. 4. This photoinduced acceleration can be quantified by the ratio of the relaxation times under UV illumination and in dark (τ_{UV}/τ_{DK}), which is, within our experimental accuracy, independent of T and on the order of 0.2. This is in qualitative agreement with interfacial shear rheometry (ISR) measurements on a PA4 Langmuir film in the same illumination conditions: *trans* PA4 shows a predominantly elastic modulus, which decreases by a factor of ~ 7 upon isomerization—as shown in Fig. 4, bottom right panel [14]. We speculate that, in our case, the elasticity of the polymer could be responsible of the mechanism postulated by Bouchaud and Pitard [38]. However, a quantitative comparison of the results is difficult and the relation between $|G^*|$ and the nondiffusive dynamics observed by XPCS is not trivial [39].

We also performed measurements under visible light, which is known to increase the polymer’s shear modulus on the macroscopic scale probed by the ISR technique. Surprisingly we found a *decrease* of the relaxation time comparable or even larger than that obtained by UV illumination (Fig. 4, bottom left). We speculate that this may be explained by the

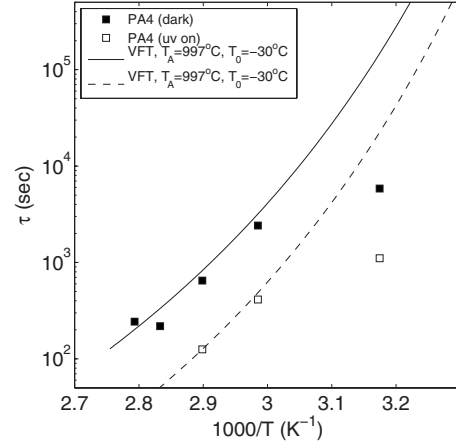


FIG. 5. Arrhenius plot of relaxation time (τ) in dark and under UV illumination, at $q=0.09 \text{ nm}^{-1}$. Lines are the VFT laws discussed in the text.

different length scales involved by the two different techniques: XPCS selects a length scale smaller than $\sim 150 \text{ nm}$, while ISR is sensitive to macroscopic (millimeter) length scales. The isomerization cycles induced by the visible light illumination (both *cis* to *trans* and *trans* to *cis* isomerization processes have approximately the same efficiency at this wavelength) may have different effects on different scales: while the local scale dynamics becomes faster due to increased molecular motion (and hence XPCS relaxation time shortens), on the macroscopic scale the film stiffens because of the reduction of defects and grain boundaries, similarly to what happens after a thermal annealing process.

Finally we analyzed the temperature dependence of the relaxation times, as shown in the Arrhenius plot of Fig. 5. We compare our data with the Vogel-Fulcher-Tammann (VFT) law

$$\tau = \tau_{\infty} \exp\left(\frac{T_A}{T - T_0}\right) \quad (3)$$

describing the bulk viscosity of PA4 ($T_0 = -30 \text{ }^{\circ}\text{C}$, activation temperature $T_A = 997 \text{ }^{\circ}\text{C}$) [16] which was confirmed by EPR, depolarized micro-Raman and quartz crystal microbalance experiments [9]. Inspection of Fig. 5 suggests that the same VFT law may be obeyed by XPCS relaxation time both in dark and under UV illumination, with the exception of the lowest temperature (42 °C). Even if this observation is based on data from a very limited temperature range, an analogous result was found by ISR also at temperatures closer to T_g : in that case the temperature dependence of the dynamic shear modulus was described by the same VFT law in dark and under UV light— T_0 and T_A being the same for the two cases, only the prefactor being affected by the photoperturbation [14]. This can be rationalized considering that T_0 and T_A reflect properties intrinsic of the glassy matrix, which are determined in our case by the acrylate main chain, and are therefore independent of photoperturbation, while the prefactor accounts for some frequency of attempt to rearrange, which in our case must be due to the most mobile part, i.e. the side chain, and is therefore obviously affected

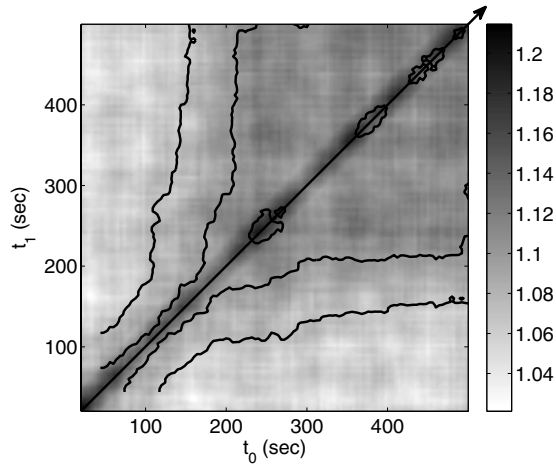


FIG. 6. Two-times correlation function during the *cis*-to-*trans* transformation at 72 °C. UV light was switched off at the initial time $t_0=0$. The arrow indicates the diagonal along which ageing time increases.

by its shape i.e., by the isomerization state. A different situation is encountered at the lowest temperature, at which a crossover from diffusive to hyper diffusive regime is sometimes observed [31], however, we also believe that the slow dynamics may start approaching the long-time stability of the experimental setup, which is limited by phenomena such as the drift of the synchrotron x-ray beam (for the dark data) or radiation induced damage of the sample for the UV case.

Out of equilibrium dynamics. In this section the photosensitivity of molecular films of PA4 is exploited to drive the system out of equilibrium and to study the dynamics in this state. To characterize the out of equilibrium dynamics, as pioneered by Sutton and co-workers [22,23,29], the usual time averaged correlation function has to be substituted by a two-times correlation function $g(q, t_0, t_1)$ defined as

$$g(q, t_0, t_1) = \frac{\langle I(q, t_0)I(q, t_1) \rangle}{\langle I(q, t_0) \rangle \langle I(q, t_1) \rangle}. \quad (4)$$

In Fig. 6 we report $g(q, t_0, t_1)$ in a typical out of equilibrium situation when the photoperturbation is switched off. Larger values of correlation are represented by darker shades, as displayed in the grayscale. In this representation, the ageing time t_{age} is given by $(t_0+t_1)/2$ (i.e., proportional to the displacement along the diagonal indicated by the arrow in the figure) while the lag time t is given by the absolute difference $|t_1-t_0|$ (i.e., the distance of a point from the diagonal). Stationary equilibrium dynamics would correspond to contour lines running parallel to the diagonal. On the contrary, as it is the case in the figure, contour lines moving away from the diagonal vs age indicate a slowing down of the dynamics. This is caused by switching off the UV photoperturbation which leaves the system to relax back towards its equilibrium *trans* configuration where the relaxation is much slower, see Fig. 4.

A useful measure of the fluctuations of two-times correlation functions is provided by the normalized variance $\chi(q, t)$ defined as in Ref. [24],

$$\chi(q, t) = \frac{\langle g^2(q, t_0, t_0 + t) \rangle_{t_0} - \langle g(q, t_0, t_0 + t) \rangle_{t_0}^2}{[g^{(2)}(q, t=0) - 1]^2}, \quad (5)$$

where the average $\langle \dots \rangle$ is performed on all the initial times t_0 while the zero time correlation $g^{(2)}(q, t=0)$ provides the appropriate normalization.

This quantity depends obviously on q and on the delay time t , and is in many ways similar to the dynamical four-point susceptibility $\chi^{(4)}$ that has been widely studied in glassy materials to characterize spatial heterogeneity in their dynamics [40,41]: while the quantity χ measured by XPCS characterizes temporal heterogeneity and $\chi^{(4)}$ characterizes spatial heterogeneity, the two are related noting that an increasing length scale over which the dynamics is cooperative would imply fewer dynamically independent scattering sites in the given scattering volume and therefore an increase in temporal fluctuations measured by χ [29]. Specifically, in the case of homogeneous diffusion dynamics, χ is independent on the delay time, while an increase in χ has been identified as a signature of growing dynamical correlation lengths in a range of disordered systems approaching arrest, such as supercooled liquids near the glass transition and granular materials near the jamming transition.

However, when the system is off equilibrium several factors might contribute to χ . In particular in the case shown in Fig. 6, the slow evolution of the correlation function as a function of the ageing time can be understood in terms of the general slowing down of the dynamics of the system after switching off the photoperturbation. This slow evolution of the degree of correlation g at fixed lag time needs to be removed before χ is calculated, therefore it is fitted by a phenomenological least squares spline approximation and subtracted. In Fig. 7, top panel, we report the evolution of χ for different values of q , as a function of lag time t for PA4 at 72 °C in dark and under UV illumination. A well defined peak in χ centered at time τ_c and with amplitude $\chi^* \chi(\tau_c)$ emerges when the sample is exposed to UV light. No similar peak was observed in dark at any q or at any temperature. Focusing on the UV data, the characteristic time τ_c follows a similar scaling relation $\tau_c \approx q^{-1}$ as the relaxation time τ (bottom left panel). The ratio τ/τ_c is about 5 like in previous experiments [28] on ageing colloidal systems. We also followed the q dependence of the intensity of the peak χ^* (bottom left panel), which is expected to be inversely proportional to the number of independent regions in the scattering volume that are responsible for the observed dynamical heterogeneity. We find $\chi^* \propto q^{-3}$, which is reasonable assuming the characteristic size of the regions to be proportional to the length scale probed ($d=2\pi/q$) at each momentum transfer q .

In Fig. 8 we summarize the results of our analysis of the dynamics in the transient phase induced by the UV photoperturbation, which was switched on at time $t_{\text{age}}=0$. In the top panel we show the variance χ for different values of t_{age} : the characteristic time of the peak position τ_c —shown in the bottom left panel—increases at early age, reaching a stationary value after about 200 seconds while the peak amplitude χ^* —bottom right panel—remains roughly constant at all ages. This is rationalized as follows: as anticipated photomechanical effects lasting about 100–200 s [34] dominate the relax-

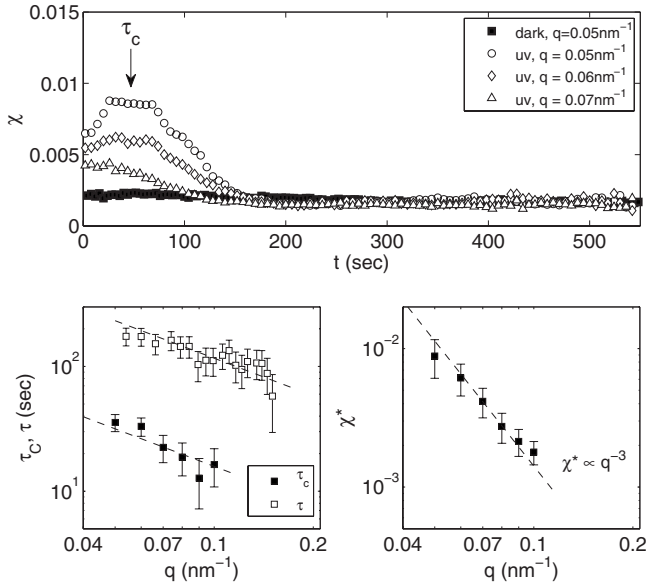


FIG. 7. Top: Variance of the two times correlation function for PA4 at 72 °C under UV illumination and in dark. Note the presence of a peak only for the UV data. Bottom left: q dependence of the peak time τ_c for the UV data compared to that of the relaxation time τ . Dashed lines indicate the $\tau \propto q^{-1}$ power laws discussed in the text. Bottom right: q dependence of the amplitude of the peak χ^* .

ation at early times, prevailing the pure diffusional motion.

At longer times these transient effects disappear and both the relaxation time and the characteristic time τ_c reach their equilibrium values, indicated by the dashed horizontal lines in the bottom left panel of the figure. We emphasize the close correspondence found in the behavior of these two in principle independent quantities. This is in some sense analogous to what observed in a different system, namely in colloidal gels recovering from shear: also in that case both times τ and τ_c follow the same law, which in that case is a linear increase with ageing time [29,42].

Concerning the measurements in dark, the absence of a peak in χ can be explained assuming that the dynamics in this case is homogeneous at least on the length scale probed in the experiment. This could arise, e.g., because the heterogeneity develops on a much slower timescale than that accessible in our experiment, or could be an effect related to the presence of the nematic potential which reduces the dynamical heterogeneity intrinsic of the supercooled glassy phase. The implications of this observation are currently under investigation.

IV. CONCLUSIONS

In this paper we have shown an unconventional application of XPCS that allows to determine local dynamical changes caused by the *cis-trans* isomerization in an azopolymer Langmuir Schaefer thin film, and we relate the findings to current theories about nonequilibrium processes in glassy systems. In particular we were able to determine the scaling

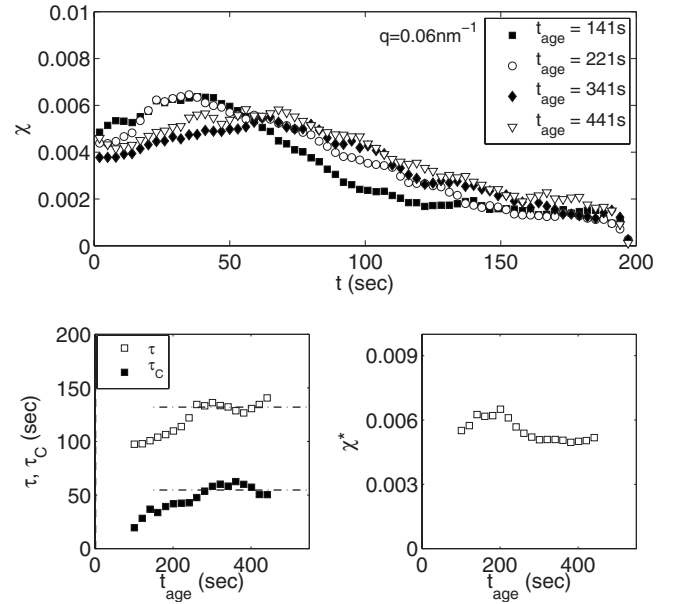


FIG. 8. Top: off equilibrium evolution of the variance χ for PA4 at 72 °C. UV photoperturbation was switched on at $t_{\text{age}}=0$. Note the shift of the peak as a function of the ageing time. Bottom left: ageing dependence of the peak time τ_c compared to that of the relaxation time τ . Dashed lines indicate their corresponding equilibrium values. Bottom right: amplitude of the peak χ^* at different ageing times.

laws for equilibrium and nonequilibrium fluctuations on local space scales (e.g., nanometers) in the long time limit (up to several hours). The data are in qualitative agreement with the random stress model developed by Bouchaud *et al.* [38] and we could bridge the gap between local and macroscopic scales by showing qualitative agreement in the behavior of the XPCS relaxation times with the light induced changes in the macroscopic shear modulus (on shorter time scales) obtained by ISR. Moreover, the temperature dependence of the relaxation times follows the same Vogel-Fulcher-Tammann law describing the viscosity of the polymer.

An accurate insight into the nonequilibrium dynamic of the system comes from the analysis of the variance of the two times correlation functions. For *cis*-PA4 it presents a peak at a characteristic time τ_c , with an inverse proportionality between τ_c and q similar to that of the relaxation time τ . These features are commonly accepted in the literature as hallmarks of heterogeneous dynamics, and have been observed previously in a few model systems. At the same time, in *trans*-PA4, no peak was observed. This is possibly due to a suppression of the dynamical heterogeneities by the presence of a nematic potential.

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