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Microscopic dynamics in nanocomposite photosensitive films studied by X-ray photon correlation spectroscopy

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Abstract

We report X-ray Photon Correlation Spectroscopy (XPCS) measurements of microscale dynamics in Langmuir-Schaeffer deposited multilayers of a photosensitive azopolymer with a low concentration of gold nanoparticles embedded. Correlation functions were measured as a function of exchanged momentum and illumination conditions (dark and UV light) and fitted with the Kohlrausch-Williams-Watts (KWW) exponential form. The microscopic dynamic of the nanoparticles was quantified, evidencing a non-Brownian superdiffusive behavior with relaxation times $\tau \approx q^{-1}$, a result analogous to what previously had been observed in the pure azopolymer [D. Orsi *et al.*, submitted to Phys. Rev. E (2010)]. Such behavior has been related to intermittent rearrangements [L. Cipelletti *et al.*, Phys. Rev. Lett. **84**, 2275-2278 (2000)] or random dipolar interactions within an elastic medium [J.-P. Bouchaud and E. Pitard, Eur. Phys. J. E **6**, 231-236 (2001)]. Photoperturbation with UV light makes the dynamics faster, in accordance with the reduction of the viscosity of the polymer found by shear rheology, but the KWW form of the correlation functions persists. At constant temperature, the dynamics of the nanoparticles embedded in the polymeric matrix is sensibly faster than the slow microscopic dynamic of the polymer. At the same time, the Vogel-Fulcher-Tammann (VFT) law for the relaxation times indicates a less pronounced temperature dependence than for the pure polymer, resulting in a slightly lower activation temperature T_A .

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1. Introduction

In recent years there has been an increasing scientific and technological interest in nanocomposite systems which combines hard and soft materials with a resulting improvement in functionalities, physical properties, and overall stability [1].

Embedding nanoparticles in a soft matrix is a common solution through which new functionalities can be achieved. Depending on concentration, dimension and composition of the nanoparticles, they can either intensively modify the dynamical properties of the system in which they are included, or just follow passively the dynamics of the surrounding material. Recently it was shown that adding Ag nanoparticles at low concentration – up to a few % in weight - in azopolymer films improves the stability of the system [2], with possible novel applications in optical recording for high-density data storage. In this case, a possible interpretation consists in a modification of the long-time dynamics of the sample induced by the presence of the nanoparticles.

On the other hand, stabilized nanoparticles at low volume fraction may be considered as passive tracers of the superdiffusive microscopic bulk dynamics observed in low-molecular-weight polymer melts [3] and in supercooled liquids near the glass transition [4].

In this work, we investigate the influence of the presence of gold nanoparticles - at concentrations below 0.1% in weight - over the internal microscopic dynamics of photosensitive polymeric Langmuir-Schaeffer films deposited on silicon. In particular, the system we investigated consists of a side-chain liquid crystalline polymer with an azobenzene moiety attached to the main chain via a flexible molecular spacer [5-7]. We employed X-ray Photon Correlation Spectroscopy (XPCS) as a tool to directly measure the microscopic relaxation times of the system in the exchanged momentum range provided by synchrotron light [8], corresponding to spatial scales of the order of 10-100 nm.

The long time dynamics of a similar sample was previously investigated in a XPCS experiment [9], observing a superdiffusive dynamics typical of colloidal gels, clays, and glasses [10-12]. The effects of photoperturbation with UV light were intensively studied, both in-equilibrium and out-of-equilibrium [13]. These studies showed a reduction of the relaxation times upon UV exposure, which is in qualitative agreement with a reduction of the viscosity of the polymer. However, the superdiffusive character of the dynamics did not change. With the present work we aim at extending our previous investigations by exploiting the larger contrast provided by the addition of the gold nanoparticles, with higher electron density, and hence a higher signal-to-noise ratio with lower incident radiation dose. It is reasonable to assume that the polymer dynamics will not be significantly affected by the addition of nanoparticles as they are stabilized to prevent aggregation, and are present at very low concentrations. Therefore, we expect to minimize problems related to radiation induced damage which was encountered in our previous experiments, especially when the sample was illuminated by UV light, while still being able to track the dynamics of the unperturbed system.

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2. Sample

The photosensitive polymer employed in this study is poly[[4-pentiloxy-3'-methyl-4'-(6-acryloxyoxyloxy)] azobenzene] (denoted PA4 in the following) which has a glass phase with $T_g = 20^\circ\text{C}$ and a nematic phase with clearing point $T_{NI}=92^\circ\text{C}$ [14]. Multilayers of PA4 were prepared by the Langmuir Schaeffer (LS) technique. Gold nanoparticles (GNP) of 5 nm nominal diameter that were stabilized by a layer of lipoic acid to avoid cluster formation following the work of Chen and Kimura [15] were embedded in the PA4 films. Single layers were prepared from a solution of PA4 and GNP in chloroform. The solution was spread on a pure water surface in a Langmuir trough and a film at surface pressure $\Pi=10\text{mN/m}$ was formed by barrier compression. Subsequently, several layers of the obtained film were deposited on Si substrates using the LS technique. The multilayer samples were checked using Scanning Electron Microscopy (SEM) to verify for their uniformity and the absence of GNP clusters. A typical SEM image of a sample with 1% weight percentage of GNP is displayed in the left panel of figure 1. Cluster of nanoparticles were not present and the particle diameter estimated from this image is in agreement with the nominal value of 5 nm, which however is very close to the resolution limit of the SEM instrument (a few nm) in this configuration. Since an accurate estimate of the GNP size is crucial for the subsequent analysis of the XPCS data, we resorted to small angle X-ray scattering (SAXS) measurements to have a more quantitative information. The right panel of figure 1 shows the SAXS pattern from the very same system as measured by SEM. We employed a Bruker D8 Discover diffractometer in a total reflection geometry, which is explained in more details in the following section, operating in the range of $1 - 5 \text{ nm}^{-1}$ in momentum transfer. For comparison we also measured the SAXS signal of a pure polymeric film (i.e. without GNPs), which is found to be much weaker. The fact that most of the SAXS signal arises from the GNPs is expected, despite their very low concentration, because of the large difference between gold and polymeric electron densities. The scattering contribution coming from the azopolymer was then subtracted and the remaining scattered intensity profile was fitted with the form factor of polydisperse hard spheres [16] to yield a mean radius $R=2.26(3)$ nm of the particles along with the width $\sigma=0.48(2)$ nm of the radii distribution and a normalized $\chi^2=1.2$.

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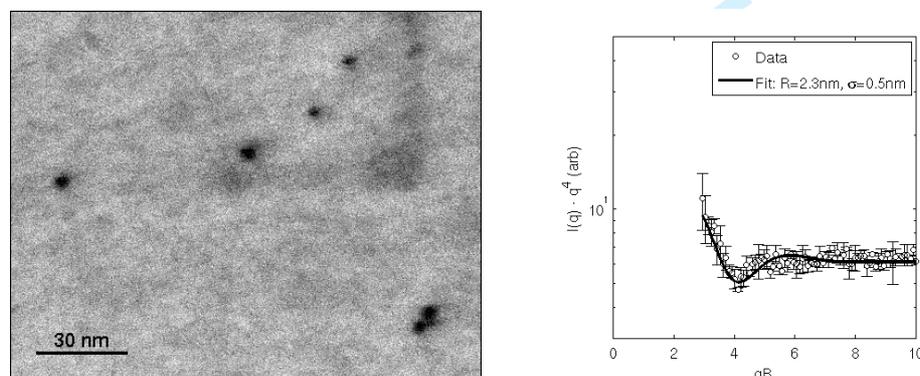


Figure 1: left SEM image of gold nanoparticles (dark dots) embedded in PA: the sample consists of 36 Langmuir-Schaeffer layers deposited on Si substrate. The particle diameter is smaller than 10 nm. The nominal weight percentage

of gold nanoparticles in PA4 is 1%. **right** SAXS measurement on the same system: the intensity $I(q)$ is fitted with the form factor for polydisperse hard spheres yielding a best fit with mean radius $R=2.26\mu\text{m}$ and polydispersity $\sigma=0.48\mu\text{m}$.

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Since PA4 contains the azobenzene moiety, it may experience several internal modifications as a consequence of photoperturbation. In particular its *trans* isomer presents an absorption peak in the UV region of the spectra. When *trans*-PA4 is exposed to light of wavelength around 390 nm it switches to *cis*-PA4, with a subsequent reduction of the dynamic shear modulus [17] and a decrease of its microscopic relaxation times [9]. Measurements in bulk are made difficult by the short penetration depth of UV light in PA4 which prevent uniform photoperturbation of the sample, showing the necessity of performing this type of measurements on a multilayer.

The samples for XPCS consisted of 75 molecular layer thick Langmuir-Schaeffer multilayers on a silicon substrate. This thickness was chosen to minimize surface effects, such as the presence of a dead layer which affects the first nanometres of thickness, and at the same time to ensure homogeneous exposure to the UV radiation. Samples were characterized by null-ellipsometry, SEM and AFM microscopy, evidencing a typical total thickness of 150nm and a mean roughness of about 1 nm, values consistent with previous measurements on similar samples [18,19].

XPCS measurements were performed at 40 °C and 52 °C with 0.10% weight concentration of GNP and at 60 °C and 72 °C with 0.05% GNP. Even if we used two different concentrations, both of them are sufficiently low to not alter the mechanical properties of the GNP/polymer composite which are the same as in the pure polymer at these low concentrations [20-22], thus leaving only temperature and illumination as parameters governing mechanical properties. On the contrary, for higher GNP concentrations, in the regime of a few percent and above, mechanical properties of GNP/polymer composites are known to be altered in a progressive way as the concentration is increased [20-22]. This is known in general for many GNP/polymer combinations, furthermore we characterized the interfacial shear modulus G^* for our particular case of GNP/PA4 for different concentrations up to 5%, finding that G^* is not affected by the presence of GNP for concentrations below 0.5% in weight [23].

3. Experimental setup

Experiments were conducted at the ID10A beamline of the European Synchrotron Radiation Facility, employing partially coherent X-rays at 8.06 keV with a relative bandwidth $\Delta\lambda/\lambda \approx 10^{-4}$. Higher energy X-rays were suppressed by a Si mirror placed after the monochromator, while slits blades with highly polished cylindrical edges defined a transversely coherent beam of size $10 \times 10 \mu\text{m}^2$. Diffraction fringes coming from the beam-defining slits were blocked by a system of guard slits placed between the sample and the beam defining aperture. The sample was placed in a vacuum chamber equipped with thermal control and a high power UV LED array (395nm) for sample illumination.

The experimental geometry (figure 2) was chosen to improve the photoperturbation efficiency while minimize beam damage effects on the sample. Similar strategies have already been adopted in previous experiments [9,24]. The sample, mounted vertically in the vacuum chamber, was aligned forming an angle of 0.15° with respect to the incident beam, well below the critical angle for total

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external reflection from the silicon-air interface at 8.06 keV ($\alpha_c=0.22^\circ$). This condition minimizes radiation damage to the sample caused by photoelectrons coming from the Si substrate, allowing at the same time measurements of small angle scattering around the strong specular reflection, which is blocked by a beam stop.

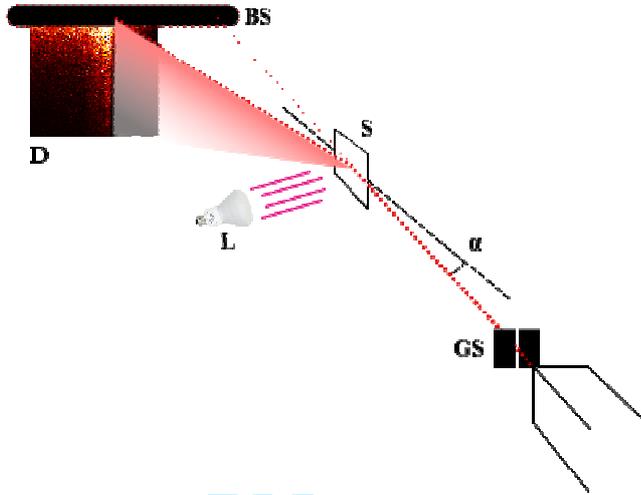


Figure 2: experimental setup. The incoming and reflected x-ray beams are indicated by dotted lines. Two guard slits (GS) block the interference fringes from the beam defining aperture (not shown). The sample (S) is aligned at an angle of $\alpha = 0.15^\circ$ with respect to the incident beam. The beam stop (BS) blocks the specular reflection while the detector (D) collects diffusely scattered radiation.

The diffuse scattering from the sample was collected by a 2D detector (MAXIPIX) -- placed 2.2 m downstream from the sample -- consisting of an array of 256x256 pixels, each of size $55 \times 55 \mu\text{m}^2$. The minimum exposure time is 1 msec, however we typically used an integration time of 100 msec in order to increase the detector signal. To follow slow dynamics, on the scale of several hours while minimizing radiation damage effects, a waiting time of 1-4 seconds was introduced between successive frames. During these intervals, a fast shutter placed upstream of the sample was protecting it against beam damage effects. All the measurements reported here are performed in equilibrium conditions, i.e. allowing a suitable waiting time after the application of photoperturbation or of any temperature variation. The onset of a stationary equilibrium regime was checked by a careful analysis of two times correlation function, as described in [9,25].

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For the data analysis we proceeded as follows: first, individual pixels of the detector were grouped in several "coarse-grained" iso-q rings (typically 20). Subsequently, we considered the temporal evolution of the intensity detected by each pixel i , computing both mean values I_i and standard deviation δ_i . Finally, we excluded from every ring those pixels with I_i or δ_i significantly different from the average values $\langle I_i \rangle$ and $\langle \delta_i \rangle$ calculated on the total number of pixels in the considered ring. On the remaining pixels the intensity auto-correlation functions $g^{(2)}(q, t)$ are then calculated as

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

$I(q, t_0)$ is the intensity measured at time t_0 and wave vector q ; the average $\langle \dots \rangle$ is performed over all the pixels in the q -bin and over all times t_0 , since we are interested in equilibrium dynamics.

4. Results

4.1 Thermal equilibrium

The diffuse scattering around the specular reflection was measured with the sample at several temperatures, in dark and under UV illumination. As discussed in section 2, most of the scattered signal originates from the gold nanoparticles, because of their higher electron density.

The correlation functions, exemplified in the left panel of figure 3, were fitted by a Kohlrausch-Williams-Watts (KWW) modified exponential form:

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

where A is the baseline, typically equal to unity, and is the contrast of the correlation function which in this geometry is around 0.3.

The characteristic relaxation time τ usually follows a power law as a function of q with exponent n , $\tau \propto q^{-n}$ while the parameter γ is the KWW exponent. In the case of Brownian diffusion, i.e. for low concentration colloidal particles moving in a simple viscous fluid, $n=2$ and $\gamma=1$ are observed.

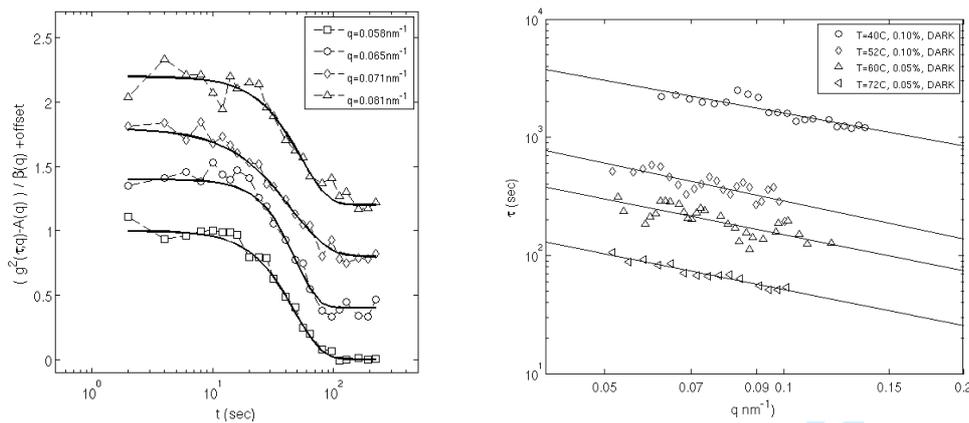


Figure 3, left: normalized correlation functions measured in GNP/PA4 in dark, at $T=72^\circ\text{C}$. Data are shifted for clarity. **Right:** relaxation times τ as a function of the exchanged momentum q , at several temperatures in absence of illumination. Data are fitted with a power law dependence $\tau \propto q^{-n}$ (continuous lines).

In the right panel of figure 3 we report the relaxation time τ measured as a function of momentum transfer q at several temperatures, with concentrations of gold nanoparticles in PA4 lower than 0.1 % in weight. An increase in temperature reduces the relaxation times while the slope of the curves remains unchanged. Figure 4 shows the results of fitting the correlation function with the KWW exponential form. While the dynamics of the nanoparticles becomes faster as the temperature increases, the q -dependence of the relaxation times remains q^{-1} (Fig. 4, left panel). On the other

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hand, the KWW exponent γ is q -independent and close to 1.5 (right panel). These results are very similar to what we recently measured in a XPCS experiment on multilayers of pure PA4 [9], suggesting that the dynamics of nanoparticles can be used to investigate the internal dynamics of the polymer, in analogy with previous measurements on glassy polymer melts [3]. This is particularly true given that the GNP concentration is low enough to leave the mechanical properties of the polymer unaffected [20-22].

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A similar superdiffusive behaviour of nanoparticles in a two-dimensional polymeric environment was found in Ref. [26] where gold particles moving in a polystyrene film were investigated by XPCS.

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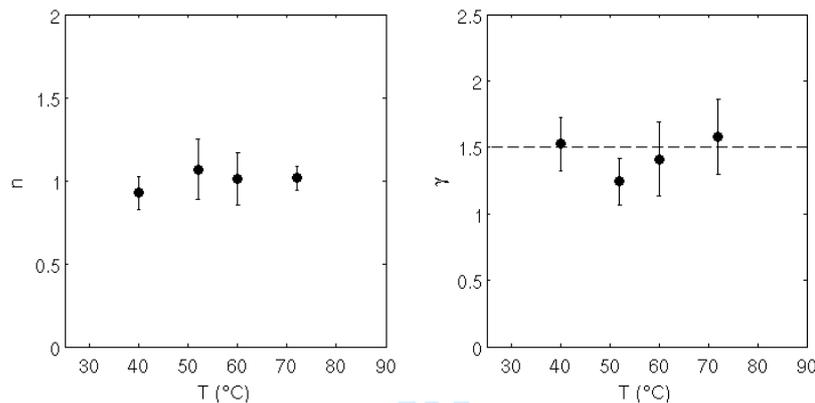


Figure 4: left Temperature evolution of the exponent n at different illumination conditions; right γ averaged over the investigated q range; the dashed line is guide to the eye.

In figure 5, the relaxation times measured at $q=0.09 \text{ nm}^{-1}$ as a function of temperature are shown in an Arrhenius plot and compared to analogous data for pure PA4. The motion of gold nanoparticles in the azopolymer is sensibly faster, with a reduction of relaxation times of about one order of magnitude respect to that measured for the pure azopolymer.

Data were compared with the well-known Vogel-Fulcher-Tammann law:

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

The curve for the nanocomposite system (continuous line) is characterized by a less steep temperature dependence represented by a lower activation temperature ($T_A=800 \text{ °C}$) with respect to the curve previously measured in bulk and in molecular layers for pure PA4 (dashed line, $T_0=-33\text{°C}$ and $T_A=997\text{°C}$).

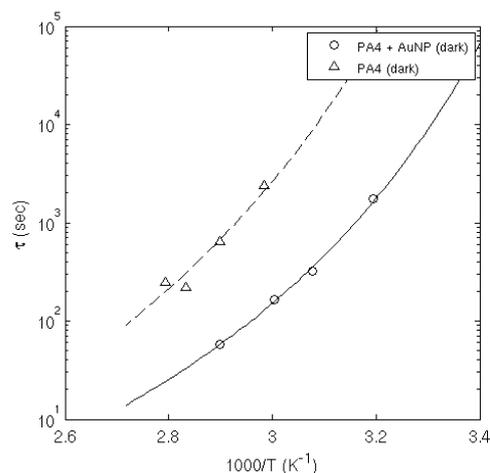


Figure 5: Arrhenius plot of the relaxation times of the nanocomposite system in absence of illumination, compared to the relaxation times of pure PA4. Data are measured at $q=0.09\text{nm}^{-1}$ and lines represent the VFT law.

4.2 Photoperturbation with UV light

Subsequently, we investigated the effect on the dynamics of the nanoparticles caused by photoperturbation with UV light at $\lambda=395\text{ nm}$. The power density of UV light on the sample was 1 mW/cm^2 while the temperature was set to 40°C with 0.1°C accuracy. In order to allow the system to reach equilibrium conditions with UV exposure, the correlation function measurements were started a few minutes after switching the light on. An analysis of two-time correlations for representative values of q confirms that the system has reached indeed a stationary state. In figure 6 we report the characteristic relaxation time τ as a function of the momentum transfer q measured both in dark and under UV illumination. The dynamics is accelerated by a factor of 30, in qualitative agreement with the fluidification effect of UV light on a PA4 layer observed by Interfacial Shear Rheology and XPCS [9,17].

The q -dependence of the relaxation times is linear even under UV light (open circles and continuous line in Fig. 6), in quantitative accord with previous XPCS results for pure PA4 [9]. This underlines our previous statement that the motion of the nanoparticles reflects the internal dynamics of the azopolymer, even when the system is suddenly illuminated by UV light.

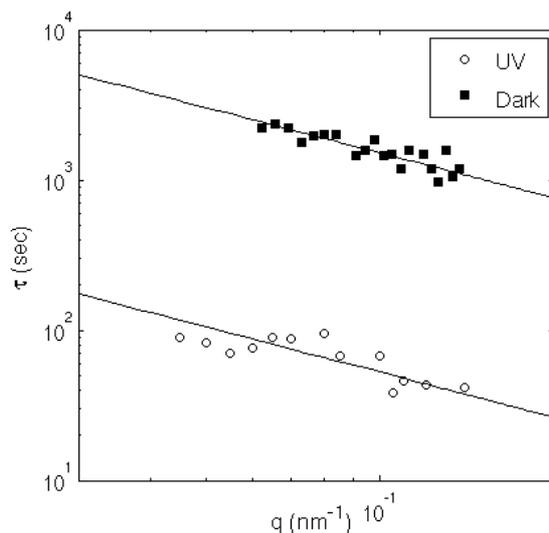


Figure 6: relaxation times of the nanocomposite system in dark (black squares) and under UV illumination (open circles, at $T=40^{\circ}\text{C}$). Data are compared with *inverse* (q^{-1}) dependencies (solid lines). The acceleration of the dynamics of the gold nanoparticles is a consequence of the photoinduced fluidification of PA4.

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By fitting the KWW expression to the correlation functions we found that the parameters γ and n are not significantly affected by the photoperturbation. However, at constant temperature, the dynamics of the polymer/GNP system is sensibly faster than that of the pure polymer, and this holds both in dark and under UV illumination. This indicates that, while photoperturbation induces the well known fluidification with the resulting reduction of relaxation times, on the other hand this process does not alter the superdiffusive behavior- which is speculated to originate from dynamical heterogeneities.

5. Conclusions

We have characterized microscopic dynamics in gold-nanoparticle and photosensitive azopolymer mixtures by X-ray Photon Correlation Spectroscopy measurements. Correlation functions were measured as a function of exchanged momentum and illumination conditions (dark and UV light) and fitted with the Kohlrausch-Williams-Watts (KWW) exponential form. We found non-Brownian superdiffusive behavior with relaxation times $\tau \approx q^{-1}$, in analogy to what was observed in the pure azopolymer [9]. Such behavior has been related to intermittent rearrangements [27] or random dipolar interactions within an elastic medium [28]. Photoperturbation with UV light makes the dynamics faster, in agreement with a reduction of the polymer viscosity that has previously been measured by shear rheology [17]. Interestingly, the parameters of the KWW law of the correlation functions are not significantly affected by the photoperturbation, in agreement with the results on polystyrene/GNP mixtures reported in the literature [3], and suggesting that GNPs can be used to trace the temperature- and in our case also illumination- dependence of dynamics in polymeric

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2 systems, with the advantage of increased scattered intensity, even if the absolute values of the
3 relaxation times are affected by the presence of the GNPs.
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