

Glass Transition and Relaxation Following PhotoPerturbation in Thin Polymeric Films

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In this letter we employ null ellipsometry on Langmuir Blodgett multilayers of a glass forming photosensitive side chain polymer to investigate both the structural changes and the related time relaxation as a function of temperature and sample thickness following isothermal optical perturbation. Below a thickness of a few layers the glassy multilayer system collapses to a smecticlike crystal. This effect is discussed in the context of the glass transition in restricted dimensionality.

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The nature of glass transition [1] is still imperfectly understood in bulk systems, and even less is known about the effects of system size and of the surfaces on the transition, although many experimental approaches have been pursued, in porous systems [2] and in thin films [3–6]. The experimental verification of the existence of the so-called cooperatively rearranging regions [7–9] is one motivation for studying systems of restricted size or dimensionality. The length scale of the cooperative behavior is expected to increase as T_g is approached, resulting in an increase of some typical relaxation time. Such a process would be disrupted as the correlation length crosses the system size.

Thus the study of thin films is particularly interesting because of good control and continuous variation of the size of the system without changing boundary conditions. Most of the experimental approaches on these systems, however, focus on the time scale of the relaxation inherent in glass transition or on the structural properties after a given equilibration time. Furthermore, as the thickness is reduced to a few molecular sizes, structural and dynamical effects of the interaction with the substrate might become so strong as to hide and/or modify considerably the intrinsic behavior of the film. For instance, maximizing the interaction of poly-(2)-vinylpyridine with a polar substrate results in a 40 °C increase of T_g [5], while a decrease of T_g is observed in thin free standing polystyrene films [4] and polystyrene on silicon [3]. Therefore another motivation for the study of thin polymer films is a fundamental understanding of substrate and interfacial interactions.

In this Letter we address these issues for the case of the glass forming photosensitive side chain polymer (SCP) produced as Langmuir-Blodgett monolayers and multilayers. We take advantage of the photosensitivity of the azobenzene moiety in poly[[4-pentyloxy-3'-methyl-4'(6-acryloxyoxyloxy)]azobenzene] (PA4) [10] to induce a perturbation in a thermally equilibrated glass film. Bulk PA4 exhibits a nematic-to-glass transition with $T_g = 20$ °C as confirmed by a variety of techniques: DSC, DMA, and ESR [11], fluctuation raman spectroscopy (FRS) and quartz crystal microbalance (QCM) [12], and birefringence [13]. Moreover, the effect of the UV illumination (the *trans* isomer absorption is

peaked at $\lambda \approx 360$ nm) is that of inducing *trans* to *cis* isomerization of the azobenzene side group [14] which is linked to the main polymeric chain via a flexible spacer of six alkyl units. The presence of such spaces allows a description of the system in terms of two fluids: the backbones and the photosensitive side chains. On the time scale of the *trans-cis* photoisomerization process, these two fluids may—to a good approximation—be viewed as independent. Thus this type of polymer has two distinctive features relevant to glass transition in restricted dimensionality systems: the possibility of taking the side chain fluid out of equilibrium by optical perturbation, and thus perform isothermal relaxation measurements, and the possible decoupling of the azobenzene moieties from the substrate; the main chains would act as the anchored template which contains the side chain fluid.

The observed effect of UV illumination of PA4 multilayers is to induce a marked increase of film thickness and a decrease of index of refraction—as detected by null ellipsometry—which are caused by the optically induced azobenzene side chain *trans* to *cis* isomerization; these processes are connected to molecular reorientation as probed by pump-probe FRS experiments in bulk PA4 [12]. Measurements have been performed as a function of temperature, number of deposited layers, and substrate preparation. To a first approximation the time evolution of the index of refraction n probes the fraction of azobenzene groups in the *cis* configuration, while the film thickness probes the (photoinduced) disorder and corresponding changes in the excluded volume. We believe this is the first time that ellipsometry in a time resolved mode has been used to obtain simultaneously both static and dynamic behaviors in a glassy system.

The multilayers were deposited either on clean Si (100) surfaces, covered by natural oxide (typical thickness 20-30 Å), or on silanized hydrophobic Si. Substrates were accurately characterized prior to film deposition. PA4 multilayers were prepared by means of the horizontal deposition [Langmuir Schaeffer (LS)] [15] technique. A chloroform solution, 1 mg/ml of PA4, was spread on high purity water, and the interfacial layer was then slowly compressed up to a typical deposition pressure

$\Pi = 15$ mN/m. We chose a Langmuir trough with a large width/length ratio in order to avoid high surface pressure gradients, which otherwise result in irreproducible isotherms and low collapse pressure. Moreover, care was taken to avoid any exposure to even the faint UV light from normal fluorescence lamps during and after film deposition. Deposited multilayers were left to equilibrate for 12–24 hours at room temperature prior to characterization.

We independently measured the anisotropic index of refraction of a ten layer PA4 film by means of spectrophotometric ellipsometry operating in the range $\lambda = 200$ –1400 nm. We obtained $n_e = 1.70$ and $n_o = 1.54$ for the out-of-plane and the in-plane propagating light (at $\lambda = 632.8$ nm), respectively. The macroscopic anisotropy of the pristine film probably originates from the LS deposition technique, in which the side chains are likely to be oriented perpendicularly to the air/water interface [16,17] by the applied surface pressure. In the following we discuss the measurements made with a high precision null ellipsometer [18] operating at fixed wavelength ($\lambda = 632.8$ nm). Because of the geometry chosen for the experiment (angle of incidence $\Phi = 50^\circ$) for the index of refraction we measure an effective average value $\bar{n} \approx \frac{1}{3}(2n_e + n_o)$.

We characterize the glass transition in our polymeric film by means of standard plots of film thickness vs temperature T . In Fig. 1 we report the T dependence of the thickness per layer of a $n = 10$ multilayer of PA4 on a clean Si (100) surface during a slow cooling ramp (rate = $0.5^\circ/\text{min}$). The measured ellipsometric angles Δ and Ψ were inverted to the index of refraction and thickness in a standard (Fresnel) manner assuming a semi-infinite Si substrate covered by a 23 \AA thick natural oxide layer and finally the PA4 film under study. The crossover, which is also evident in the raw data, between the two linear dependences of film thickness vs temperature is generally used to determine the glass transition temperature T_g [3]. The result of such a measurement depends on the

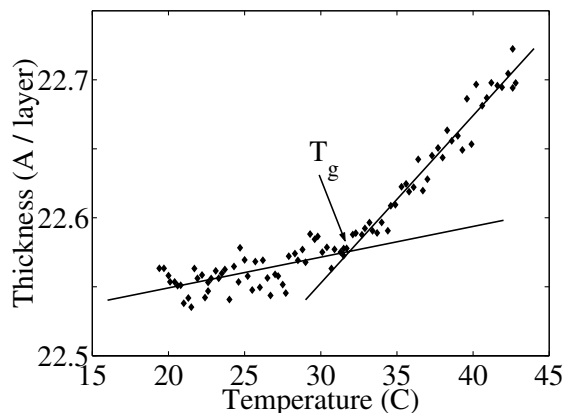


FIG. 1. Temperature dependence of the thickness per layer of a PA4 multilayer. The crossover between the two linear dependences marks T_g .

time allowed for the equilibration at each temperature (or on the speed of the temperature ramp applied). To avoid this possible problem, in our system we suggest a different way of measuring T_g , i.e., by monitoring the amplitude of the equilibrium photoinduced expansion. The advantage of this is the decoupling of the relaxation time from the equilibrium configurational change, which is the quantity reported in Fig. 2. The occurrence of T_g is indicated by the onset of the decrease, with increasing temperature, of the photoexpansion. In fact at low temperatures (at and below T_g) the back-to-equilibrium relaxation process is effectively frozen, so that the optically induced stationary state corresponds to the maximum expansion. This explains the saturation of the photoinduced thickness change at low temperatures. Above T_g the relaxation time window becomes comparable to that of the photoisomerization process, and, as the temperature increases, the relaxation becomes more effective, therefore the net photoexpansion decreases. The transition temperature T_g for a $n = 10$ multilayer as measured with both techniques agrees, resulting in $\approx 10^\circ\text{C}$ higher than in bulk (where $T_g = 20^\circ\text{C}$ [10]).

In Fig. 3, we report a typical time evolution of both the index of refraction n (top) and thickness (bottom) for a ten layer film. The sample was brought from room temperature (RT) to the desired temperature ($T = 40.0 \pm 0.1^\circ\text{C}$) (see the initial variation of n and t in the first 200 sec of Fig. 3), then it was left to equilibrate and was exposed to UV illumination by means of a suitably filtered Hg lamp (λ band = 362 ± 5 nm). UV illumination clearly induces *trans* to *cis* isomerization, resulting in a marked increase of film thickness and a decrease of index of refraction (due to the lower polarizability of the *cis* isomer). Under the experimental conditions reported here, most of the azobenzenes have been converted to the *cis* configuration. For details see forthcoming reports [13].

Coming now to the dynamics of relaxation, we find that in the temperature range of our study (limited by T_g on

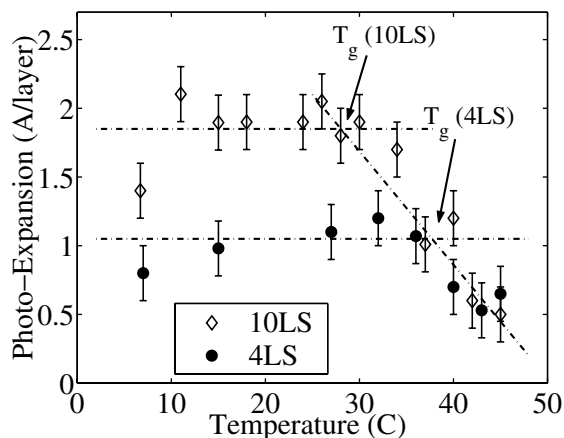


FIG. 2. Photoinduced expansion per layer of two different multilayers (four and ten layers) of PA4 as a function of T .

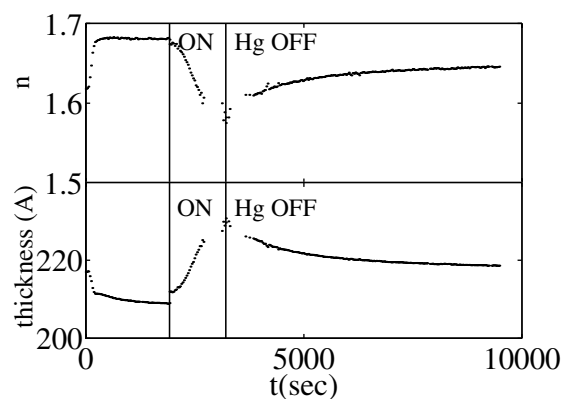


FIG. 3. Time evolution of index of refraction n (top) and film thickness (bottom) at $T = 40^\circ\text{C}$. Vertical lines mark the ON and OFF switching of the Hg lamp.

one side and by the photoinduced isotropization temperature [13] on the other) it follows a standard Kohlrausch-Williams-Watts [19] stretched exponential law with the exponent β ranging from 0.6 to 1.0, and the relaxation time τ was found to follow the usual Vogel-Fulcher-Tammann law [20]

$$\tau(T) = \tau_0 \exp\left(\frac{T_a}{T - T_0}\right).$$

Thus from all points of view, both static and dynamic, our system conforms to the classical phenomenology of a glass in the neighborhood of T_g . For instance, on the $n = 10$ multilayers, by fixing the activation temperature for the *cis-trans* isomerization to the value determined by DMA [11] $T_a = 1270$ K, we obtained $T_0 = 230 \pm 10$ K, in agreement with the results obtained by FRS and QCM ($T_0 = 220 \pm 20$ K) [12] and DMA ($T_0 = 243 \pm 3$ K) [11].

As stated at the beginning of this paper, the index of refraction n probes the fraction of azobenzene groups in the *cis* configuration (therefore a local quantity) (space scale of the azobenzene subgroup ≈ 1 nm) while the photoinduced increase of the film thickness is related to the increased excluded volume (therefore a more delocalized property). We find that both quantities have the same behavior. We can exclude a spurious correlation due to the ellipsometric technique, which could hold for the thinner films but not for films of ten or more layers. Moreover, some measurements were also confirmed by the spectrophotometric ellipsometer technique. Thus the marked similarity between the time evolutions of index of refraction and film thickness suggests that mechanical measurements (such as QCM and film thickness measurements) probe essentially the same type of dynamics as do local measures (e.g., the index of refraction n). Therefore from all points of view our sample shows the normal behavior of a glassy system approaching the glass transition temperature.

We come now to what is perhaps a most remarkable result: it concerns the strong divergence of the relaxation time τ as the number of layers was decreased below a

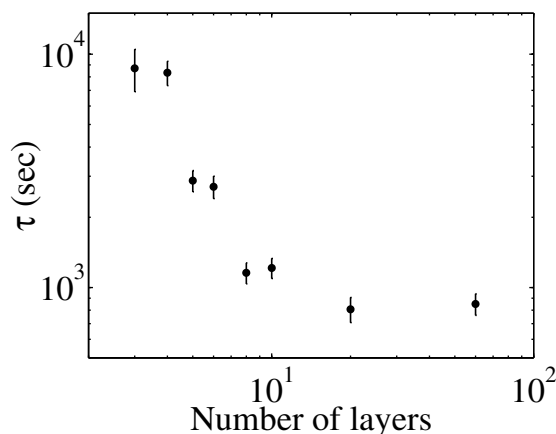


FIG. 4. Back-to-equilibrium relaxation time τ (sec) at constant temperature (40°C) as a function of film thickness.

critical value of about 10 (see Fig. 4). The same phenomenology was observed in PA4 multilayers deposited onto hydrophobic (silanized) Si substrates. As the size of the system crosses the correlation length appropriate to the sample temperature, it is expected in fact that the disruption of cooperativity yields a decrease of τ . To understand the fundamental mechanism by which size influences τ , we can take advantage of the fact that the motion of the side chains, due to the presence of the flexible spacer, is relatively independent of the main chains and their anchoring to the substrate.

We assume that the side chains at the air/water interface point upward as reported for other azobenzene SCP [16,17]. A single layer of PA4 as deposited shows an effective thickness of $25\text{--}27$ Å corresponding to almost the full side chain length (≈ 28 Å). Multilayers (>4 layers) have a typical thickness of $21\text{--}22$ Å per layer. The difference is most likely due to partial interdigitalization of the side chains and/or to kinks in the alkyl chains, as, e.g., in [21]. This is confirmed by preliminary x-ray reflectivity and grazing incidence diffraction. For $n \geq 10$ multilayers the temperature dependence of the thickness is similar to that shown in Fig. 1.

However, when a film made of a few layers ($n = 4$) is cooled below RT, a new phase is stabilized, with a remarkable decrease in thickness (17 Å/layer, Fig. 5) and a very high index of refraction. We ascribe this to the onset of a smecticlike crystal stabilized by the LS deposition. Clearly the dynamics in such a compact phase is much more hindered than in the normal glassy phase. In our case this could provide a physical interpretation for the so-called dead layer which has been phenomenologically introduced in other polymeric thin films [22,23]. We propose that below RT we have a crossover from a quasicrystalline to a glassy phase as a function of film thickness. Moreover, for the $n = 4$ sample at low temperatures the optical pump induces a transition from the smecticlike crystal to a glass. On the contrary, at high temperatures ($T > T_g$) or for larger number of layers the sample is already in a disordered phase, which is only perturbed by the

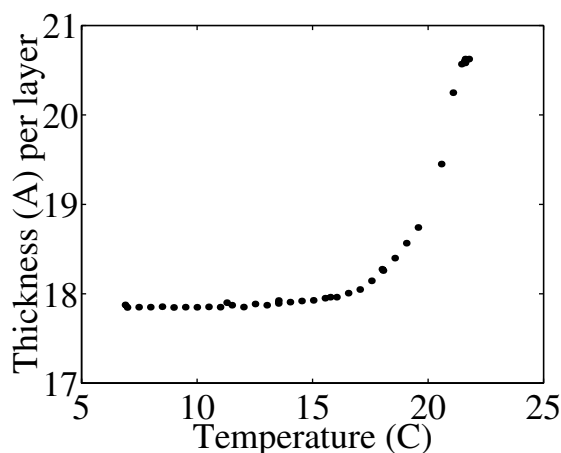


FIG. 5. Temperature induced contraction of an $n = 4$ multilayer of PA4 cooled below RT.

photoisomerization. Moreover, we demonstrate that such effects are intrinsic to the structural behavior of the multilayers, and independent of the hydrophobic or hydrophilic nature of the substrate. The overall situation resembles that of other liquid crystalline SCP in bulk, where an increasing order of the mesophase is associated with a decreasing mean lateral distance of the mesogenic units (e.g., with higher density) and a larger activation energy barrier for the mesogenic (β) relaxation [24].

The formation of a highly ordered phase for the first layers, the propagation of this order, and the slowing down of the relaxation time τ can possibly be due to a combined effect of (A) interaction with the substrate, which is most probably of a geometric nature, since substrate hydrophobization does not affect the observed phenomenology, and (B) mesogenic potential, responsible for the propagation of the order: from the onset of the sharp increase of τ we may infer a rough estimate of the correlation length which is about 2–3 layers (of the order of 50 Å), a value consistent with that quoted, e.g., in [23].

In conclusion we have shown that a photosensitive SCP as PA4 can be quite useful in studying isothermal relaxation phenomena in the glass transition range, especially when thickness effects are investigated. In particular we have shown that below a thickness of a few layers the glassy multilayer system collapses to a quasicrystalline structure. This behavior might not be specific to the compound we studied, since we have seen that it is probably due to geometric factors, and not related to surface treatment of the substrate. More generally, our results indicate that the glassy phenomenology exists for all thicknesses, as long as the temperature is above T_g ; the more ordered phase is found only at lower temperatures and for sufficiently low thickness. This effect could be quite general and should be taken into account in interpreting results on ultrathin glassy phases.

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