

# Looking for the glass transition in a single molecular layer on the water surface

L Cristofolini<sup>1</sup>, P Cicuta<sup>2</sup> and M P Fontana<sup>1</sup>

<sup>1</sup> Dipartimento di Fisica and Istituto Nazionale di Fisica della Materia, Università degli Studi di Parma, via delle Scienze, I-43100 Parma, Italy

<sup>2</sup> Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK

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## Abstract

We present here results which indicate that polymeric monolayers confined at the air–water interface may provide interesting model systems for the study of glass transition phenomenology in a strongly confined 2D geometry. We report on photoinduced relaxation of the pressure–area isotherms in Langmuir monolayers of a photosensitive polyacrylate, using null-ellipsometry to study the evolution of the film thickness in the neighbourhood of the bulk glass transition. Furthermore, viscoelastic behaviour is investigated by a combination of surface quasielastic light scattering and expansion–compression isothermal cycles.

## 1. Introduction

For both practical and fundamental reasons, the study of so-called nanostructured glasses has been pursued strongly in recent years [1]. Glasses can be viewed as natural randomly nanostructured systems, and possibly many of their fundamental properties are closely tied to space–time inhomogeneities in their response functions on the nanoscale. However, glasses can also be produced in specific nanostructures, either in the form of ultrathin films [2] or as nanoparticles [3]. It is the interplay between this externally imposed ordering on the nanoscale, and the random inhomogeneities which naturally characterize glasses, which brings much theoretical and experimental interest to the study of the effects of confinement on the nanoscale.

In recent work we have used the *trans*–*cis* photoisomerization transition in a polymer with the azobenzene moiety in the side chain to take the system out of equilibrium and then study the isothermal back-relaxation process. In particular we studied Langmuir–Blodgett (LB) [4] multilayers and other more complex architectures of a photosensitive side-chain polyacrylate, namely PA4, in which the *cis*–*trans* photoisomerization transition of the azobenzene moiety in the side chain drives several optical, mechanical, and structural effects, which have been extensively studied, both in bulk, where the material behaves as a fragile glass former with  $T_g \approx 22^\circ\text{C}$  [5–8], and in the confined geometry of ultrathin films, down to one monolayer [9, 10]. In this latter case an important issue is that of isolating the intrinsic

effects of nanoconfinement on the glass transition from the effects due to interactions with the substrate and to the presence of a free surface.

We found that the pristine films had a layered structure up to 4–6 layers thickness; successively deposited layers did not yield any periodicity in the  $z$ -direction, or any crystalline ordering in the  $x$ – $y$  plane, at least at room temperature. Thus even the pristine films, for a sufficiently high number of layers (say more than 20), could be considered glassy. In any case the entire multilayer can be converted to a glassy state by heating above the solid–nematic phase transition and cooling down below  $T_g$ , or by isothermal optical pumping of the photoisomerization transition. This is important since to study the effects of nanoconfinement we are mainly interested in very thin films, say from one to ten monolayers thick. Another important point that we have addressed is the effect of interactions with the substrate and of the presence of the free surface on the observed phenomenology. In particular, the effect of the presence of the free surface was investigated by studying PA4 multilayers covered by a top bilayer of barium behenate, or superlattices made of replicas of that structure [11].

In this work we wish to push the nanoconfinement to its extreme limit, and at the same time, we hope, do away with the problems of extrinsic effects: thus we present a study of the Langmuir molecular monolayer trapped at the air–water interface. Certainly a single molecular layer confined to the flat plane of the air–water interface is as close as we can get to a two-dimensional system. In most cases (especially with the classic simple fatty acid molecules) the compressed Langmuir monolayer can be viewed as a polycrystalline system. The situation becomes different for more complex molecules such as polymers: in this case the molecular fluid is non-Newtonian, relaxation times are slow, and the fluid is disordered. The questions are: Is it a glass? Does it have a glass transition? What is the role in all this of the restricted dimensionality? In this paper we present some experimental results which should allow a preliminary assessment of these questions: we apply the ellipsometric thickness relaxation technique already demonstrated for LB multilayers [9] to monitor photoinduced thickness changes on the Langmuir compression isotherms of PA4 monolayers; we study their metastability by means of surface pressure–area hysteretic cycles.

We expect that in the compressed monolayer the interactions between the side chains will dominate, yielding the effective two dimensionality of the molecular relaxation, and the possibility of glassy behaviour. At lower densities instead we would expect an essentially two-dimensional fluid of more independent particles. Finally, we probe dissipation and viscoelastic behaviour by means of surface quasielastic light scattering (SQELS) [12], using photon correlation spectroscopy.

## 2. Experimental procedures and data analysis

The liquid crystalline polymer used was poly[[4-pentyloxy-3'-methyl-4' (6 acryloxyxyloxy)] azobenzene] (PA4). Its synthesis and main characteristics are described elsewhere [7]. Here we recall only that its calorimetric glass transition temperature  $T_g$  is 21 °C, with a melting temperature of 78 °C, and a nematic phase ending at the clearing point temperature of 96 °C [7]. Upon cooling, the nematic fluid of the azobenzene side chains undercools all the way down to  $T_g$ . In our case the samples had a molecular weight  $M_w = 19\,000$  (weight averaged) and  $M_n = 12\,000$  (number averaged).

In a typical experiment, 100  $\mu\text{l}$  of hexane:benzene (1:2) solution with 0.33  $\text{mg ml}^{-1}$  of PA4 was spread on high-purity water (MilliQ,  $\rho > 18\ \text{M}\Omega\ \text{cm}$ ); the Langmuir layer was then slowly compressed either in dark (*trans* isomer), or under the light from a high-pressure Hg lamp, whose maximum emissivity is peaked at  $\lambda \sim 350\ \text{nm}$ , in order to study the effect of UV illumination (*cis* isomer). From UV–visible absorption spectra taken for deposited LB films

we can state that 90% of the azo moieties undergo photoinduced *trans*-to-*cis* isomerization after illumination in the conditions of the present experiment.

We have also studied layers of monomeric azo-acrylate (henceforth labelled monomeric A4), i.e. monomers that upon polymerization would lead to the polymeric PA4, and layers of mixed composition—in the latter case the two solutions were mixed in controlled proportions prior to the dispersion on the Langmuir trough.

Layer thickness was measured by high-precision null-ellipsometry at  $\lambda = 633$  nm, well away from the absorption peaks of both the isomers of PA4. The incidence angle was  $\Phi = 48^\circ$ ; we measured both ellipsometric angles  $\Delta$  and  $\phi$ , the latter only as a check, as for very thin films the only meaningful information is contained in  $\Delta$ , whose time evolution gives us an indication of the back-to-equilibrium relaxation process following photoperturbation. In a typical experiment, the film was formed and compressed to  $\Pi = 10$  mN m<sup>-1</sup> at a given temperature, in the dark. Then UV perturbation was applied for a given time, and back-to-equilibrium relaxation was followed both by null-ellipsometry, as in [9], and by measuring the surface pressure using a Wilhelmy plate.

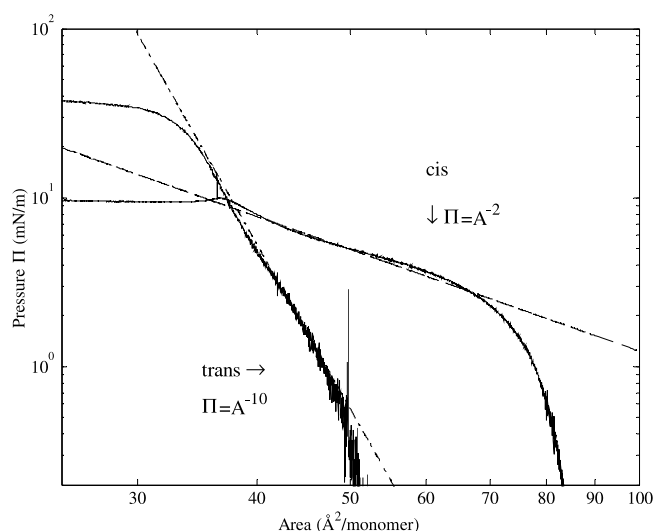
The power spectrum of light scattered inelastically from the capillary waves (thermal roughness) on a liquid surface can be resolved with photon correlation spectroscopy. This technique allows the non-invasive measurement of the surface tension of a liquid and, if a uniform surface monolayer is present, the power spectrum can be analysed to extract the dilational elasticity and viscosity of the monolayer. This is possible for a range of surface parameters such that a strong coupling exists between in-plane and transverse fluctuation modes [13]. The SQELS set-up and data analysis methods used in our experiments have been described previously [14]. In the experiments reported in this paper, an attenuated 30 mW He:Ne laser (633 nm) was used, illuminating a region of about 5 mm diameter on the liquid surface. The scattering angle was fixed, thus selecting the surface mode of wavevector  $q = 306$  cm<sup>-1</sup>, which on the bare water surface has a frequency of  $\sim 45$  kHz. Correlation functions have been measured as a function of molecular area. In the data analysis, following the theoretical description in [15], the value of the surface tension was fixed to the value measured with the Wilhelmy plate.

### 3. Results

#### 3.1. Compression isotherms and cycles of Langmuir monolayers

The results obtained for deposited LB multilayers suggest that the azobenzene side chains may form an effectively two-dimensional fluid when dispersed at the air–water interface. Again most of the interaction with the substrate, which in this case is the aqueous subphase, would involve the polymeric main chain. An added advantage of the Langmuir monolayer is that its two-dimensional density can be varied at will by compressing the barriers. In particular, this implies the tunability of the relative weight of intramolecular interactions and interactions with the subphase. In a previous preliminary work [11] we have shown that a scaling analysis [16] can be applied to these isotherms. In the semidilute regime the surface pressure can be expressed as  $\Pi = \Gamma^y$  where  $\Gamma$  is the concentration of monomers per unit of surface area, and  $y$  is a scaling exponent related to the Flory exponent  $n$ , which in turn relates the chain radius of gyration  $R_g$  to the number of monomers  $N$  [17, 18]. The Flory exponent  $n$  is connected to  $y$ . In particular in two dimensions one expects  $n = 1$  for the extended chain, and a decrease to  $n = 4/7$  for  $\theta$ -solvent, and to  $n = 1/2$  for poor solvent conditions. Correspondingly  $y$  takes the values of 2, 8, and infinity.

In figure 1 we show the  $\Pi$ - $A$  isotherms in scaling form for the monolayer in the dark and after illumination by filtered UV light. The scaling picture emphasizes dramatically the effects



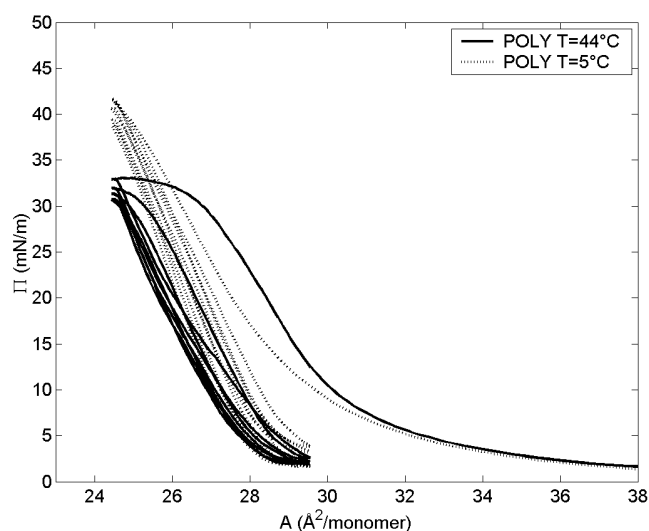
**Figure 1.** The scaling law for the compression isotherm of PA4 measured at  $T = 21\text{ }^{\circ}\text{C}$  with and without UV photoperturbation. Dashed lines correspond to the scaling laws  $\Pi = A^{-y}$  with  $y = 2$  and  $10$ , typical of very favourable interaction with the subphase and of almost  $\theta$ -solvent conditions respectively.

of the *trans*–*cis* photoisomerization on molecular interactions with the air–water interface. In particular we note that the scaling exponent changes from about ten to two upon optical pumping; this implies a change in the interaction with the aqueous subphase, from a situation almost of theta solvent to that of good solvent, respectively. Such behaviour can be understood on the basis of the difference between the properties of the azobenzene side chain in the two configurations: the *cis* isomer has a strong dipole moment  $\sim 3\text{--}5\text{ D}$ , in contrast to the  $0.5\text{ D}$  for the *trans* isomer. Thus the combined action of hydrophilic *cis* isomers in the presence of a polyacrylate main chain results in chain swelling as in good solvent conditions.

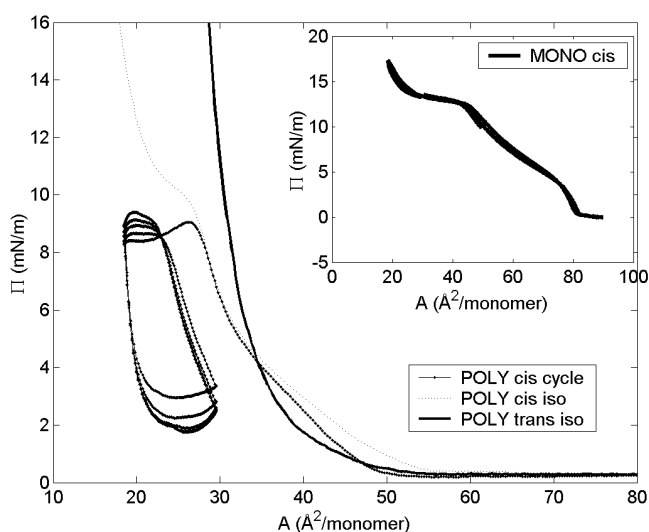
We therefore conclude that the air–water interface is a good solvent for PA4 in *cis* form, whereas it is a theta solvent, or even a bad solvent, for the equilibrium, *trans*, configuration.

In order to investigate the viscous behaviour connected with the presence of the main polymeric chain, we performed expansion–compression cycles on Langmuir monolayers of PA4, both in *trans* and in *cis* form (therefore in good and not good solvents respectively), and, for comparison, of monomeric A4, i.e. in monolayers consisting of the same molecular species, but not linked as a polymeric chain, again both in *trans* and in *cis* form.

In figure 2 we report the  $\Pi$ – $A$  isotherm cycles obtained from the Langmuir monolayers of polymeric PA4 in *trans* form: we find a small hysteresis, whose amplitude is comparable to the effects of collapses probably due to the morphology of the film, which consists of patches: these collide unavoidably during compression, even at the slowest speeds (down to  $2\text{ mm min}^{-1}$ ). We also note in the following cycles a very steep increase and decrease in the  $\Pi$ – $A$  isotherm, even steeper than the slope for the first compression (which is already steep, giving rise to the coefficient  $y = 10$ , as mentioned above in the scaling analysis). This extra toughness observed during following compressions might arise from the formation of a closely packed, dense, and strongly entangled polymeric layer. As air–water interface is a bad solvent for PA4 in the *trans* configuration, after its first compression, the compressed aggregates do not dissolve during the following expansions, giving rise to a stable isotherm, in which the only notable evolution upon cycling is related to small collapses.



**Figure 2.** Compression cycles for polymeric *trans* PA4 at different temperatures. We observe a relatively small hysteresis, whose amplitude is comparable with the effects of collapses, which are probably due to patches crashing during compression.



**Figure 3.** The expansion–compression cycle for polymeric PA4 in *cis* form at  $T = 5^\circ\text{C}$ , together with the isotherms measured for the same substance both in *cis* (dashed curve) and in *trans* (continuous curve) configurations. Note the different slopes of the leftmost and of the rightmost parts of the cycle: on compression (right) the slope of the cycle resembles closely that of the isotherm in *cis* form; on expansion (left) the slope is that of *trans* PA4. Inset: the same cycles, but for monomeric A4, in *cis* form: no hysteresis is observed at any pressure.

In the *cis* form, however, the same polymer exhibits very large and stable (at least at low temperature) hysteretic cycles, as can be seen from figure 3. In contrast, monomeric A4 has absolutely no hysteresis, as shown in the inset of the same figure, figure 3, when in the *cis* form, at any pressure, and almost none in the *trans* form, except above  $20\text{ mN m}^{-1}$ , nor

does it have the collapses shown by the polymeric *trans* form. This is what is expected for a non-viscoelastic monolayer.

Looking at the wide and stable cycles of polymeric *cis* PA4, two considerations occur to us: we confirm that the air–water interface is a good solvent for PA4 in *cis* form, as expansion of the compressed monolayer causes its dissolution; moreover, careful inspection of the same figure, figure 3, shows that the slope of the  $\Pi$ – $A$  curve in the hysteretic cycle on compression (rightmost part) resembles closely that of the isotherm of PA4 in the *cis* configuration, whereas on expansion after compression (leftmost part) the slope of the cycle resembles that of the isotherm of *trans* PA4. From this, it is tempting to conclude that compression forces the azo moieties back to the *trans* configuration. If this were to be confirmed (say by independent UV–visible absorption measurements on the Langmuir monolayer, which are already planned), this would lead to the first evidence of mechanically induced back-isomerization of an azo dye.

The area within each loop corresponds to the energy dissipated by the system in a cycle, which turns out to be about  $E = 4$  meV/monomer; it is tempting to associate this quantity with the energy for the *cis*–*trans* isomerization cycle under UV illumination. This quantity is much smaller than the activation energy for the *cis*–*trans* back-isomerization in the dark ( $E = 109$  meV [5]), as is reasonable, since in the present case the UV illumination puts the azo moieties in the electronic excited state in which isomerization is most likely to happen.

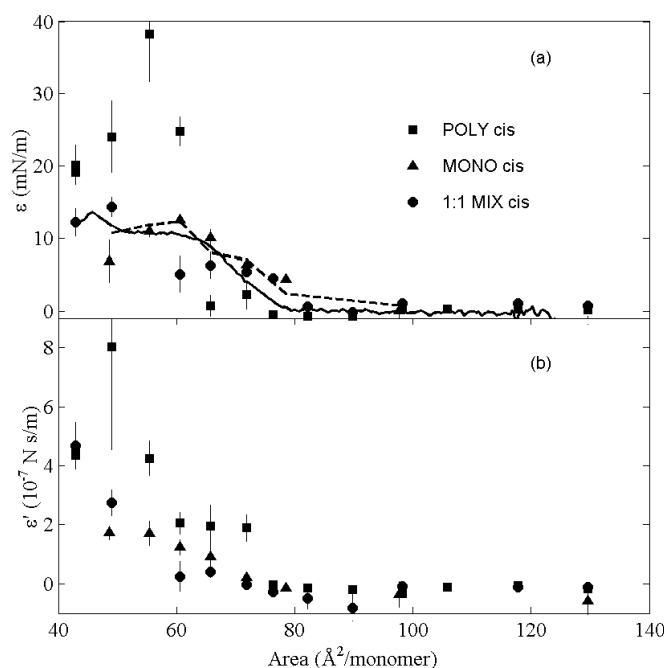
### 3.2. Surface quasielastic light scattering

The Langmuir isotherm and cycles can yield only indirect proof of viscoelastic behaviour of the film under study, and can only provide a measurement of the static compressional modulus  $\varepsilon_{stat} = \Gamma(\partial\Pi/\partial\Gamma) = -A(\partial\Pi/\partial A)$ , i.e. the modulus at zero frequency. In order to measure directly the relevant viscoelastic parameters of the Langmuir monolayer, we have used a totally different technique to study relaxation and dissipation in the Langmuir monolayer, i.e. quasielastic light scattering in the reflection mode. As stated, this technique allows the direct measurement of the time-dependent thermal roughness correlation function, and hence the determination of the monolayer viscoelastic properties.

In figure 4(a) we report the compression modulus  $\varepsilon_0$  for the polymeric PA4, for its monomer, and for a 1:1 mixture of polymer and monomer, in the *cis* form, as a function of the area per monomer. For comparison the static compressional modulus of the polymer and that of the monomer,  $\varepsilon_{stat}$ , are also shown. The high-frequency and static quantities agree substantially for the system in *cis* form, at least for areas bigger than  $60 \text{ \AA}^2/\text{monomer}$ . This is expected when the system is purely elastic, whereas  $\varepsilon_0(\omega) > \varepsilon_{stat}$  for dissipative viscoelastic systems.

In figure 4(b) we report the related SQELS viscous modulus  $\varepsilon'$ , whose values are not very large, in agreement with the essentially elastic character of the *cis* film. Whereas the elastic modulus is essentially the same for monomeric and polymeric systems, it is interesting to note that below  $70 \text{ \AA}^2/\text{monomer}$  the viscous modulus (imaginary part) for the polymeric PA4 abruptly increases to larger values than for the monomeric A4; this can be interpreted by taking it that the polymeric backbone introduces extra friction and dissipation mechanisms with respect to a film made of monomeric units alone. In this respect it is interesting to note how the 1:1 mixture behaves exactly as the pure monomeric film: the fraction of monomeric units acts as an effective lubricant. It would be interesting to explore different compositional ranges.

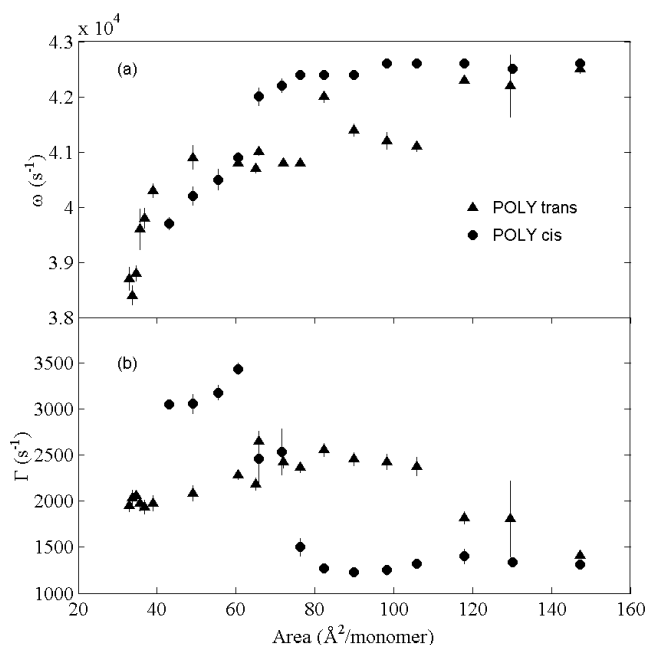
In figure 5 we compare the SQELS data for the *trans* and *cis* isomers of the polymeric PA4. Fitting the *trans* isomer data by fixing the static value of the surface tension was found to give unphysical values for the elastic moduli. Furthermore, fitting with the tension as a



**Figure 4.** (a) The compression modulus  $\varepsilon_0$  as measured by means of SQELS at  $T = 21$  °C for both polymeric and monomeric A4 and their 1:1 mixture, in *cis* form, together with the static modulus  $\varepsilon_{stat}$  (continuous curve for polymeric PA4, dashed curve for monomeric A4). (b) The compressional viscosity  $\varepsilon'$  for polymeric and monomeric A4 and their 1:1 mixture.

free parameter (a fit that robustly provides the tension but loses accuracy on the elastic moduli values) showed that the tension fluctuates both in time and between adjacent positions along the isotherm. This is evidence of inhomogeneous patches forming in the monolayer, and prevents us from analysing the *trans* isomer SQELS data with the microscopic model. Data were instead fitted to extract the frequency  $\omega$  and damping  $\Gamma$  of the thermal roughness, as this fitting requires no assumptions. Figure 5(a) shows the fitted values of  $\omega$  as a function of area. The frequency of the capillary waves depends to first order on the surface tension. As the monolayer is compressed, the scatter in the frequency  $\omega$  for the *trans* isomer is evidence of patches, and the decrease of the frequency below  $80 \text{ \AA}^2/\text{monomer}$  reflects the upturn in the pressure isotherm. Figure 5(b) shows the fitted values of the damping  $\Gamma$  as a function of the area per monomer. The damping coefficient depends on the degree of coupling of in-plane and out-of-plane surface modes. We find that there is much less coupling for the *trans* isomer at areas below  $70 \text{ \AA}^2/\text{monomer}$  than for the *cis* isomer. This (noting that the corresponding  $\omega$ -values are very similar) indicates that the *trans* isomer is far more rigid than the *cis* form. It is commonly accepted in the literature [6, 19, 20] that isomerization causes fluidification of azo polymers, although no quantitative direct data have been published so far. Here we have a clear observation of this fact.

In conclusion, our SQELS data indicate the rigid character of the film in *trans* form, thus directly confirming our findings on the hysteretic cycles found in the isotherms. Similar behaviour to that of *trans* polymeric PA4, albeit at a qualitative level, was encountered in Langmuir monolayers of polymeric brushes, in their glassy state [21].

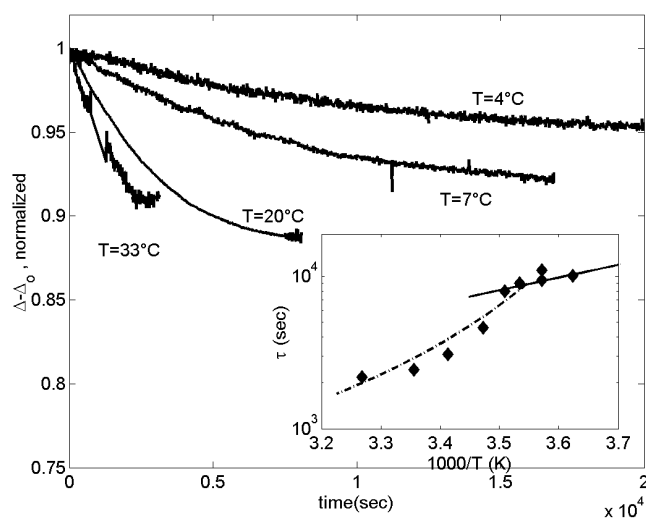


**Figure 5.** The area dependence of the frequency  $\omega$  (top panel, (a)) for both the *trans* (triangles) and *cis* (circles) isomers of polymeric PA4, and the area dependence of the damping  $\Gamma$  of the thermal roughness (bottom panel, (b)) for both the *trans* and *cis* isomers of polymeric PA4.

### 3.3. Ellipsometric measurement of structural back-to-equilibrium relaxation

The experimental picture that we have presented so far indicates that the Langmuir monolayer could be viewed as a possible glassy system: therefore we have applied to the Langmuir monolayer confined at the air–water interface the same pump–probe ellipsometric technique as we used for the PA4 LB layers [9], and studied the isothermal back-relaxation of the monolayer thickness as a function of temperature. The temperature evolution of the back-to-equilibrium relaxation process, as probed by the ellipsometer, is shown in figure 6; clearly the back-to-equilibrium relaxation time  $\tau$  increases as the temperature is lowered. The resulting values for  $\tau$  are shown in the inset of the same figure 6, for several temperatures in the range of the bulk  $T_g$ . There are two main problems in trying to obtain information from these data: one of course is the large error, and the other is the limited temperature range which was technically accessible to our apparatus in its present form. In the figure we report possible best fits to the data using a Vogel–Fulcher–Tammann (VFT) function with  $T_0 = 233$  K (in agreement with the values found in previous works [5, 7]) down to a  $T_g$  of about 286 K, and an Arrhenius plot ( $T_A = 1920$  K) for below this temperature. However, it is very difficult to differentiate the quality of the present fit from that of a purely Arrhenius plot over the whole temperature range studied. The same problem applies to the determination of the relaxation time  $\tau$ : the stretched exponential fit is only slightly better than the purely exponential one. We must note however that in the case of a purely Arrhenius fit, the activation temperature should be about 6000 K, which is five times more than  $T_A$  determined by DMA measurements for bulk PA4 [7]. We therefore discard the purely Arrhenius fit, in favour of the VFT–Arrhenius description. At present however, the only reasonable conclusion that we can draw from these measurements is that it is possible to make them, but some substantial improvements in the experimental apparatus are needed before any quantitative conclusions can be drawn.





**Figure 6.** The back-to-equilibrium relaxation process for the monolayer thickness, as measured by null-ellipsometry, at the indicated temperatures. Inset: characteristic times  $\tau$  for the back-to-equilibrium relaxation, plotted against the inverse temperature, together with a fit to a VFT law at high  $T$  (dashed curve, left) and an Arrhenius law (continuous straight line, right) below  $T = 13^\circ\text{C}$ .

#### 4. Conclusions

We feel that the experimental results presented here, and in particular the evidence of rigid behaviour in the *trans* monolayers, indicate that polymeric monolayers at the air–water interface have the potential of being interesting model systems for the study of glass transition phenomenology in a strongly confined 2D geometry. Of particular relevance is the possibility of varying continuously such a fundamental parameter as the 2D density; this allows the study of crossover from single-particle (Arrhenius) behaviour to collective glassy behaviour (if indeed such is actually demonstrated), thus separating the intrinsic characteristics of the glass transition from the other extrinsic features of the specific system under study.

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