

Revealing the respective effect of aging and cyclic deformation through the memory effect in glassy polymers

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Abstract. It has been known for 40 years that the state of a glass cannot be characterized by a single parameter such as its density and depends on its whole thermal history in a complex way. This phenomenon, known as the memory effect, reveals that the spatial distribution of the dynamics in a glass is deeply heterogeneous. Among the various memory effects, we will focus on the following one. After an annealing at a temperature T , a glassy system will exhibit a specific signature of susceptibility—around the temperature T of annealing. This effect shows that relaxations during annealing occur only in some domains of specific dynamics. This has been observed in a variety of glasses, with different techniques.

The memory effect, here, is observed for the first time through the dynamical elastic modulus. We show that the dynamical elastic modulus can be described by the simple phenomenological so-called Tool–Narayanaswamy–Moynhian (TNM) model. We evidence the competition between plastic deformation and annealing by applying cyclic strain during the annealing. As a result, we establish that deformation exhibits an effect that is opposite to thermal annealing and less selective in temperature.

Keywords: memory effects (experiment), slow dynamics and ageing (experiment), structural colloidal and polymer glasses (experiment)

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Introduction

Glasses are disordered systems with a huge distribution of relaxation times. Moreover, they are out of equilibrium and then evolve slowly towards a thermodynamic state that depends on their history. Thus they exhibit a time dependence of their macroscopic properties that is called physical aging. This time evolution is controlled by the relaxation times of the glass, that are themselves controlled by its history. Most of the time, thermal stimulations are used to probe the dynamics of glassy systems. With glassy polymers, it is possible to use mechanics as an additional stimulation degree to study glass dynamics. The effect of static mechanical stimulations on the physical aging of a polymer glass has been extensively studied by several authors (see [17], which presents a good review of the main experimental results obtained on this point). The widely held interpretation is that large stress erases aging, leading thus to a rejuvenation that would be similar to the one observed after a thermal quench [2, 18, 19]. However, the modifications induced by mechanics on the time relaxation distribution function of the glass are still unknown. Results obtained on different classes of glass (polymer or colloidal glass) showed that the effect of intermediate mechanical stimuli (i.e., in sub-yield conditions) on the relaxation times can be quite complex [2, 19]. It was indeed observed on colloidal glasses that, after such mechanical history, the glass seems to be both younger at short times and older at long times.

We want here to investigate precisely the effect of mechanics on the relaxation times of a polymer glass. In particular, we want to measure from which deformation amplitude the time relaxation spectrum of a polymer glass is modified. One way is to analyze the variations of the visco-elastic modulus of polymethylmethacrylate chains induced by a mechanical stimulus applied during a given time below its glass transition temperature T_g . Indeed, the viscoelastic modulus of a polymer $G^*(T, \omega)$ measured at the temperature T and frequency ω is controlled by the distribution function of relaxation times existing at

T [26]. The measure of the mechanical modulus is thus a good tool to probe the evolution of the time relaxation function of a glassy system.

Such an experiment requires us to submit the polymer glass to a mechanical stimulus during a given time at a given temperature below T_g . The main difficulty is that—in the absence of mechanical stimulus—the polymer glass physically ages during the isothermal step. We thus need to estimate the evolution of the time relaxation induced by an annealing step on its visco-elastic properties in order to be able to extract the modifications due to the mechanical stimulus. Moreover, we need to use a protocol allowing us to probe the largest window of the relaxation time distribution. For that purpose, we chose to adapt a procedure developed by Bellon *et al* [5, 6] on glassy polymer or by Doussineau *et al* on disordered metals [7, 8]. It consists in measuring the mechanical properties of a polymer glass along a temperature loop, cycling from a temperature T_0 above T_g to a temperature T_1 below T_g . The cooling is stopped for a given time t_{stop} during which the polymer system is kept isothermal at a temperature T_{stop} , lower than its T_g . Previous studies based on dielectric measurements performed on several glasses have shown that such method is successful in revealing the evolution of the time relaxation distribution function having occurred during the annealing. The effect of this is a change of the dielectric properties over a restricted temperature range, that depends on the temperature T_{stop} chosen for the annealing. We decided to impose a similar thermal history to cross-linked polymethylmethacrylate (PMMA) chains. But in addition, the polymer will undergo a mechanical stimulus during the annealing. We chose to apply a salvo of cyclic deformations, because after a given number of cycles, the glass reaches a stationary state. Moreover, the application of cyclic strain enables us to control the timescale of the stimulus through its frequency. We want to compare the temperature dependence of the visco-elastic modulus of the glassy polymer measured after an annealing with or without cyclic deformations. We expect thus to distinguish the effect of such cyclic mechanical stimulus on the polymer time relaxation spectrum.

In section 1, we describe the three thermo-mechanical histories that we applied to cross-linked PMMA chains. Afterwards, we will focus in section 2 on the variations of the visco-elastic modulus induced by a simple annealing. Our results are similar to the memory effects, already listed by Bellon *et al* from previous observations made through dielectric measurements [5]–[8]. According to these authors, these macroscopic modifications of the polymer response show that relaxations occurring during annealing specifically affect local domains of the glass depending on their dynamics. Thus a memory effect would be the signature of complex spatial arrangement of the dynamics, in which the typical length of relaxations depends strongly on the temperature. We will see that these experimental results can be qualitatively described by the Tool–Narayanaswamy–Moynhian (TNM) phenomenological model. This TNM approach predicts that the evolution of the time relaxation distribution shape is essentially governed by the evolution of its average relaxation time τ_0 and its width. According to this model, the state of a glass depends only on τ_0 , and thus is determined simply by the whole temperature history of the sample. Thus, it appears that the effect of simple thermal annealing can be interpreted in a simple manner. Lastly, in section 3, we will study the effect of cyclic sinusoidal deformations on the time relaxation distribution. We show that a 1% amplitude deformation is enough to induce an evolution of the glass dynamics. The mechanical stimulus does not lead to an effect similar to annealing but acts on a large domain of the relaxation spectrum.

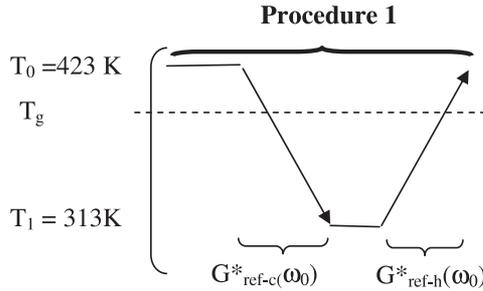


Figure 1. Schematic representation of procedure 1, applied to measure the mechanical response of PMMA chains $G_{\text{ref}}^*(\omega_0)$, that will be taken as a reference in this work.

1. Experimental procedure

In this work, we compared the mechanical response of PMMA chains having undergone three different thermal and mechanical histories. To do so, we measured the shear viscoelastic modulus along a temperature cycle from a temperature $T_0 > T_g$ to a temperature $T_1 < T_g$. In order to identify the respective effects of temperature and mechanics, we used three distinct procedures.

- Procedure 1 corresponds to a simple temperature cycle.
- Procedure 2 consists in a temperature loop with an annealing step performed below T_g during the cooling.
- Procedure 3 corresponds to procedure 2 with an additional cyclic mechanical stimulus applied during the annealing.

We will now describe the three procedures in more detail.

Procedure 1

The polymer undergoes a simple loop of temperature—shown in figure 1—cycling from a temperature above the glass transition temperature T_g denoted T_0 to a temperature T_1 below T_g . The polymer system is maintained for 30 min at both T_0 and T_1 . The temperature heating and cooling rate, $|dT/dt|$, is constant. We probed the mechanical response of the polymer chains along the temperature loop. The measurements were performed in the linear regime applying a sinusoidal strain of amplitude γ_0 at a frequency ω_0 . ω_0 is called the observation frequency.

The mechanical response measured with this procedure will be taken as a reference in the following. The corresponding shear dynamical modulus will be denoted $G_{\text{ref}}^*(\omega_0)$, adding the index ‘c’ ($G_{\text{ref-c}}^*(\omega_0)$) for the cooling step and the index ‘h’ ($G_{\text{ref-h}}^*(\omega_0)$) for the heating step (see figure 1).

In a dynamical mechanical experiment the glass transition temperature is arbitrarily assimilated to the temperature of the maximum of G'' . In the following we will call T_g the temperature corresponding to the maximum of G'' .

In this work, we took $T_0 = 423$ K and $T_1 = 313$ K. The majority of the results presented here were measured with $|dT/dt| = 0.083$ K s⁻¹, $\gamma_0 = 0.07\%$ and $\omega_0 = 1$ Hz.

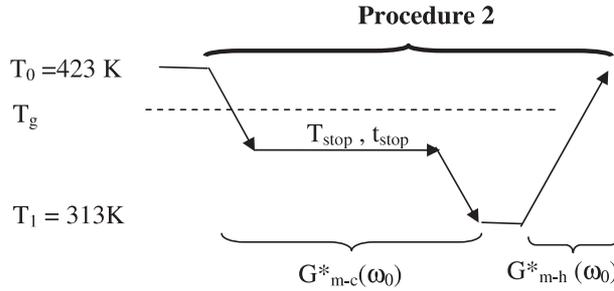


Figure 2. Schematic representation of procedure 2, applied to measure the mechanical response $G_m^*(\omega_0)$ of PMMA chains having undergone an annealing step below T_g .

Using these experimental conditions, the maximum of G'' is located around 390 K for cooling and at 400 K for heating (see figure 4).

Procedure 2

As in procedure 1, the polymer undergoes a loop of temperature, cycling from T_0 to T_1 . The polymer system is maintained for 30 min at T_0 and T_1 . The difference from procedure 1 is that the cooling is stopped for a time t_{stop} during which the polymer system is kept isothermally at a temperature T_{stop} , lower than its glass transition temperature (see figure 2). We measured the mechanical response of the polymer chains in the linear regime along the temperature loop, applying a sinusoidal strain of amplitude γ_0 at a frequency ω_0 . The corresponding shear dynamical modulus will be denoted $G_m^*(\omega_0)$, adding the index ‘c’ ($G_{m-c}^*(\omega_0)$) for the cooling ramp and the index ‘h’ ($G_{m-h}^*(\omega_0)$) for the heating ramp.

Our aim is to identify the effect of an annealing performed at a temperature T_{stop} on the visco-elastic modulus of PMMA chains. For that, we compared the mechanical responses of the polymer chains measured with procedures 1 and 2 using the same experimental conditions, i.e. same temperature rate $|dT/dt|$, and the same deformation amplitude and frequency, γ_0 and ω_0 . In order to reveal and analyze the effect of the physical aging undergone by the glassy polymer during the annealing step on the mechanical response, we have chosen to consider the ratio of the real parts $G_m'(\omega_0)/G_{\text{ref}}'(\omega_0)$ and of the imaginary parts $G_m''(\omega_0)/G_{\text{ref}}''(\omega_0)$ of the moduli $G_{\text{ref}}^*(\omega_0)$ and $G_m^*(\omega_0)$.

In practice, we compared the mechanical responses measured on the same sample with procedures 1 and 2 consecutively. We analyzed the influence of the temperature and the duration of the annealing. For that purpose, we compared the mechanical responses obtained on the same sample consecutively by varying the parameters T_{stop} and t_{stop} .

Procedure 3

Here, the thermal history undergone by the sample is the same as the one applied in procedure 2 as shown in figure 3. The difference from procedure 2 is that a salvo of mechanical cyclic deformation is applied during the annealing step. The amplitude and

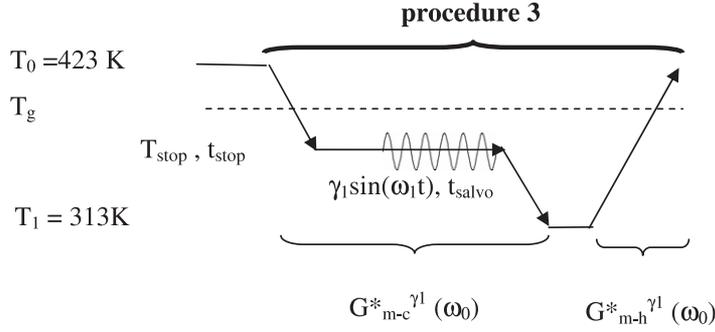


Figure 3. Schematic representation of the thermal and mechanical history applied with procedure 3. During the isothermal step at T_{stop} , a salvo of cyclic deformation of amplitude γ_1 and frequency ω_1 is applied for a time t_{salvo} .

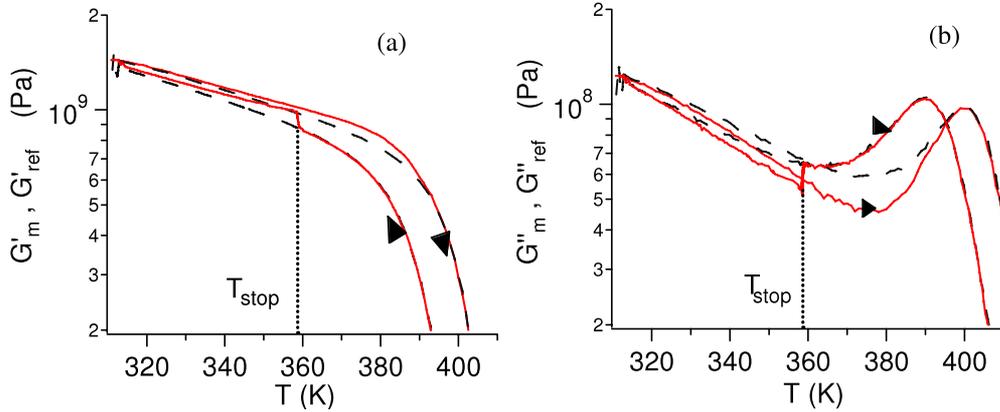


Figure 4. Variation of the real parts (a) and imaginary parts (b) of the shear modulus measured with procedure 1 (dashed line) and procedure 2 (solid line). Measurements were performed with $|dT/dt| = 0.083 \text{ K s}^{-1}$, $\omega_0 = 1 \text{ Hz}$, $\gamma_0 = 0.07\%$, $T_0 = 423 \text{ K}$, $T_1 = 313 \text{ K}$. $T_{\text{stop}} = 358 \text{ K}$ and $t_{\text{stop}} = 12 \text{ h}$.

the frequency of this cyclic deformation are denoted γ_1 and ω_1 , respectively. The duration of the salvo is denoted t_{salvo} . In this work, the deformation amplitude γ_1 applied during the salvo was chosen to be smaller than 2%.

The visco-elastic modulus, $G_m^{*\gamma_1}(\omega_0)$, is measured along the whole temperature cycle (except during the salvo of cyclic deformation), applying a sinusoidal deformation of amplitude γ_0 at a frequency ω_0 .

In order to identify the effect of an annealing combined with cyclic mechanical stimulus, we have compared the visco-elastic modulus measured with procedures 3 and 1. For that purpose, we have considered the ratio of the real parts $G_m^{\prime\gamma_1}(\omega_0)/G_{\text{ref}}^{\prime}(\omega_0)$ and of the imaginary parts $G_m^{\prime\prime\gamma_1}(\omega_0)/G_{\text{ref}}^{\prime\prime}(\omega_0)$ of the moduli $G_{\text{ref}}^*(\omega_0)$ and $G_m^{*\gamma_1}(\omega_0)$.

Afterwards, the modifications induced by the mechanical stimulus on the visco-elastic modulus were distinguished by plotting the temperature dependence of the quantities $[G_m^{\prime\gamma_1}(\omega_0) - G_m^{\prime}(\omega_0)]/G_{\text{ref}}^{\prime}(\omega_0)$ and $[G_m^{\prime\prime\gamma_1}(\omega_0) - G_m^{\prime\prime}(\omega_0)]/G_{\text{ref}}^{\prime\prime}(\omega_0)$.

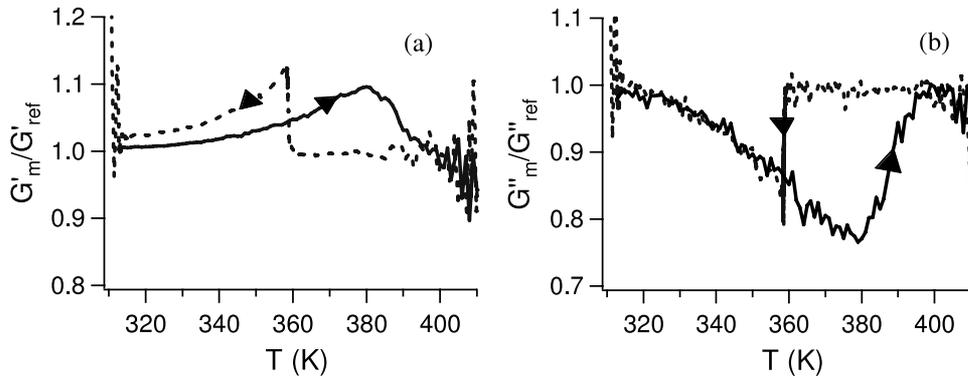


Figure 5. The evolution of the ratio of the real parts G'_m/G'_{ref} (a) and the imaginary parts G''_m/G''_{ref} (b) of the shear moduli G_m^* and G_{ref}^* measured applying procedure 2 and procedure 1, respectively. Data collected during the cooling step are shown with the dotted line while those obtained during the heating step are plotted with the solid line. Experimental conditions were $|dT/dt| = 0.083 \text{ K s}^{-1}$, $\omega_0 = 1 \text{ Hz}$, $T_{stop} = 358 \text{ K}$, $t_{stop} = 12 \text{ h}$.

All the measurements were performed on cross-linked polymethylmethacrylate (PMMA) chains in order to avoid the polymer flowing above the glass transition temperature. Measurements were realized with an RDA II rheometer, using a rectangular torsion geometry. The dimensions of the samples were $15 \times 10 \times 1 \text{ mm}^3$.

In the following, we will first analyze the changes induced by an annealing performed below T_g on the visco-elastic modulus of cross-linked PMMA chains. The experimental results and the main conclusions will be presented in section 2. Then, in section 3, we will focus on the effect of a nonlinear mechanical stimulus performed below T_g on the mechanical response of the glassy PMMA.

2. Effect of an annealing: simple memory effect measurements

2.1. Experimental results

Figures 4(a) and (b) present the characteristic variations of the real and imaginary parts of the dynamical shear modulus measured along the temperature loop. In this experiment, the isothermal step was performed at 358 K for 12 h. Figures 5(a) and (b) show the corresponding ratio of the real parts G'_m/G'_{ref} and the ratio of the imaginary parts G''_m/G''_{ref} of the moduli G_m^* and G_{ref}^* .

The annealing induces a change of the mechanical response of the glassy polymer. When cooling is stopped at T_{stop} , the real part of the modulus increases and the imaginary part decreases. When cooling from T_{stop} to T_1 is performed, the modulus G_{m-c}^* tends towards G_{ref-c}^* at $T < 330 \text{ K}$. During heating, the glass seems to keep the memory of its previous thermal history: G_{m-h}^* departs from G_{ref-h}^* by a few degrees above the isotherm temperature. The location of the deviation of G_{m-h}^* from G_{ref-h}^* depends on the temperature chosen for the isothermal step, as shown on figure 6. The amplitude of the deviation of G_{m-h}^* from G_{ref-h}^* increases with the duration of the isothermal step t_{stop} , the temperature rate dT/dt and for decreasing frequency ω_0 .

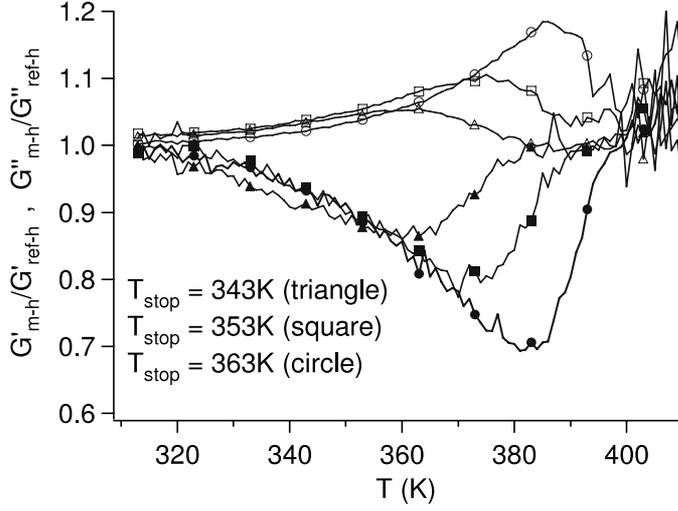


Figure 6. Dependence of the ratio of the real parts G'_{m-h}/G'_{ref-h} (a) and the ratio of the imaginary parts G''_{m-h}/G''_{ref-h} (b) on the annealing temperature T_{stop} . Data corresponding to G'_{m-h}/G'_{ref-h} are plotted with open symbols, and those for the ratio G''_{m-h}/G''_{ref-h} with filled symbols. In all cases, the duration of the isothermal step t_{stop} was taken equal to 12 h.

In the following, we will call $T_{max}^{G'}$ and $T_{min}^{G''}$ the temperatures corresponding to the maximum of G'_{m-h}/G'_{ref-h} and the minimum of G''_{m-h}/G''_{ref-h} , respectively. In figure 7, we observe that $T_{max}^{G'}$ and $T_{min}^{G''}$ increase linearly with T_{stop} .

Moreover, we performed measurements at $T_{stop} = 358$ K and $\omega_0 = 1$ Hz, varying the durations of the isothermal step from $t_{stop} = 1.5$ to 18 h. We observe in this case a weak increase of the temperature $T_{max}^{G'}$ and $T_{min}^{G''}$ (5 K for an increase of t_{stop} of a factor 12). The amplitude of the modulus deviation increases linearly with the logarithm of t_{stop} . Furthermore, the temperatures $T_{max}^{G'}$ and $T_{min}^{G''}$ and the shape of (G'_{m-h}/G'_{ref-h}) do not depend on the frequency ω_0 . Only the amplitude of the deviation increases for decreasing ω_0 .

Finally, the temperature, the maximum amplitude and the shape of (G'_{m-h}/G'_{ref-h}) and (G''_{m-h}/G''_{ref-h}) are very sensitive to the temperature rate applied over the whole thermal cycle. The amplitude of the deviation increases for larger $|dT/dt|$. $T_{max}^{G'}$ and $T_{min}^{G''}$ are shifted towards high temperature for increasing $|dT/dt|$. However, the quantity $[T_{max}^{G'} - T_g(dT/dt)]$ does not depend on $|dT/dt|$ for measurements performed applying the same temperature rate $|dT/dt|$ during cooling and heating—we recall here that $T_g(dT/dt)$ corresponds to the temperature at the maximum of G'' for the heating step measured applying a given temperature rate $|dT/dt|$.

In conclusion, thermal annealing applied below the glass transition temperature induces significant changes of the mechanical response of a polymer glass measured using sweep temperature conditions. The changes are localized on a restricted temperature range, that shifts with the annealing temperature. Such variations of the visco-elastic modulus are similar to the one listed by Bellon *et al* with dielectric measurements [5, 6] or by Fukao *et al* with differential scanning calorimetry experiments [16] using the same experimental procedures.

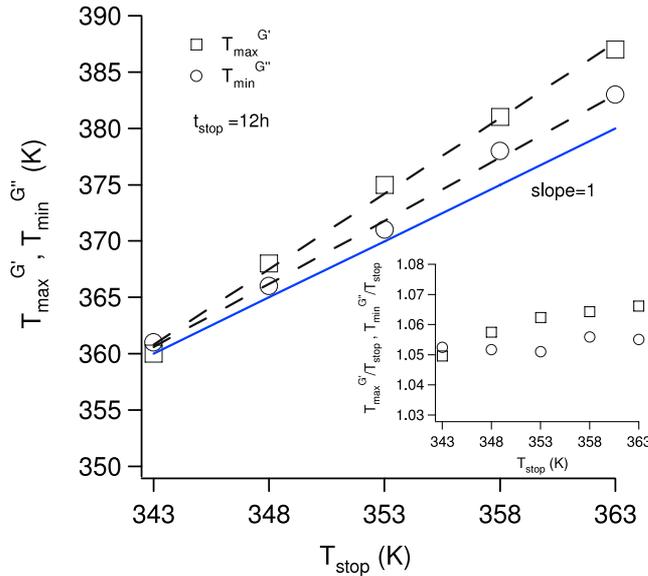


Figure 7. Variation of the temperature $T_{\text{max}}^{G'}$ and $T_{\text{min}}^{G''}$ with temperature of the isotherm T_{stop} . $T_{\text{max}}^{G'}$ and $T_{\text{min}}^{G''}$ were taken at the maximum of $G'_{m-h}/G'_{\text{ref-h}}$ and the minimum of $G''_{m-h}/G''_{\text{ref-h}}$, respectively. Data in this figure were measured with the following experimental conditions: $t_{\text{stop}} = 12$ h, $\omega_0 = 1$ Hz. In the inset, the variation of $T_{\text{max}}^{G'}/T_{\text{stop}}$ and $T_{\text{min}}^{G''}/T_{\text{stop}}$ with T_{stop} is shown. The dashed lines correspond to linear fits of the data. As a reference, we added a straight line of slope 1 (solid line).

2.2. Discussion

If a glass is kept at a constant temperature below its glass transition temperature, its relaxation spectrum drifts slowly towards slower and slower timescales during the annealing. Such a time evolution—called physical aging—is controlled by the relaxation times of the glass themselves. This last feature was clearly evidenced by Struik [1] in his famous ‘simple physical aging’ experiments performed on glassy polymers after a thermal quench. Struik observed that their dynamical properties—for instance their compliance $J(t)$ —depend on the time t_w that has elapsed from the quench to the beginning of the creep experiment. The compliance $J(t, t_w)$ of an aging glass, a signature of the time relaxation spectrum, is actually controlled by a reduced variable t/t_w^μ , where μ is an exponent of value close to 1. This behavior is observed on many other glassy systems [2] and appears to be typical of out-of-equilibrium systems that exhibit a single characteristic time that tends towards infinity.

The scaling law revealed by these Struik experiments indicates that the time distribution function of the glass is simply shifted towards long times without important modification in shape—there is no modification if the exponent μ is equal to 1. However, experiments studying the glass response after more complex thermal histories showed that aging in general cannot be described by a single relaxation time such as the average time of the time distribution, but is governed by the complex evolution of a wide relaxation spectrum [3].

Here we measured the mechanical properties of a polymer glass while sweeping its temperature over a temperature loop going from $T_0 > T_g$ to $T_1 < T_g$. Our experiments show that an annealing performed below T_g perceptibly modifies its mechanical response. The physical aging undergone by the polymer glass during the annealing step induces variations of the visco-elastic modulus. The amplitude of the modulus changes increases both with the duration of the isothermal step and the annealing temperature, in agreement with what is expected from the Struik observations. The main feature of our experiments is that the modulus deviation induced by physical aging is visible on a restricted temperature range, that shifts with T_{stop} , the temperature chosen for the annealing. Such localized variations of the glass response were observed in many disordered systems—disordered crystals [7, 8], spin glasses [9]–[12], molecular glasses [13] and polymer glasses [5, 6, 14, 15]—using dielectric measurements [5]–[8], [15], or differential scanning calorimetry [16]. This feature was baptized ‘memory effect’.

According to these previous works [5]–[16], the memory effect is a phenomenon that would reveal a deep structural heterogeneity in glasses. It would show that relaxations which occur during annealing specifically affect local domains of the glass depending on their dynamics. Thus memory effect is discussed in terms of complex spatial arrangement of the dynamics, in which the typical length of relaxations depends strongly on temperature. Models like that of Bouchaud [20], soft glassy rheology (SGR) [21], or more recently the Long model [22, 23], provide some dynamical law for the evolution from mode to mode and their coupling, with a physical approach in the latest model. Up to now, there is not any connection between the various approaches, and making such a connection is in itself huge work, beyond the scope of this paper. We restricted ourselves to describing and interpreting our result in the simplest way possible. In that respect, a class of phenomenological models that is usually referred to as the Tool–Narayanaswamy–Moynihan (TNM) model was developed relatively early to account for the out-of-equilibrium dynamics in polymer glasses (for a review, see [4]).

In this TNM model, the time relaxation distribution of a glass is described by a stretched exponential function, defined through two parameters, the exponent β of the exponential function and the average relaxation time τ_0 . The evolution of the time relaxation distribution occurring during physical aging is described by the variation of the average relaxation time τ_0 only. Moreover, τ_0 is determined in this model by temperature history. The exponent β is kept constant. The simplicity of such models allows us to reproduce the experimental conditions of procedures 1 and 2 used in this work. As detailed below, since the predictions of the TNM model reproduce all the observed phenomena, we limit ourself to a comparison between our thermal memory effect experiments and the TNM model.

We used the formulation developed by Adam, Gibbs and Fulcher for the TNM model, as detailed in the appendix, but the results do not depend on this particular choice. This model allows the calculation of a characteristic time during a complex thermal history of the system. It depends on both the temperature and the out-of-equilibrium structure of the material, which is accounted for by the so-called fictive temperature T_f , that evolves towards the equilibrium $T_f \rightarrow T$ with the dynamics of the system. The fact that the out-of-equilibrium structure could be accounted for by a single parameter is certainly the major oversimplification of this model. However, the two main features of the glassy dynamics are taken into account. Characteristic times are strongly nonlinear with respect

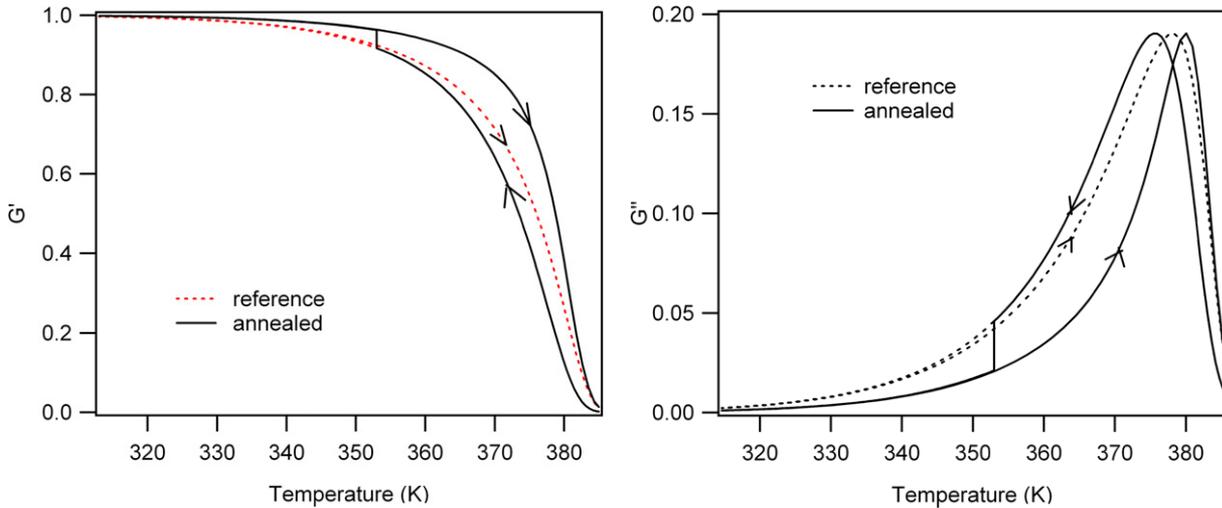


Figure 8. Storage (left) and loss (right) moduli as a function of temperature, calculated at 1 Hz as detailed in the appendix for two different thermal histories similar to the experimental conditions. The label ‘reference’ stands for a simple cooling–heating cycle (procedure 1) performed at $|dT/dt| = 0.083 \text{ K s}^{-1}$. The label ‘annealed’ stands for a thermal history where an annealing at $T_{\text{stop}} = 353 \text{ K}$ has been performed for 12 h (procedure 2).

to the structural parameters and to the temperature. Relaxation towards equilibrium is non-exponential, or, equivalently, the characteristic time distribution is wide.

The two thermal histories used in the experimental part—with (procedure 2) or without (procedure 1) an isothermal step—lead to a small difference in the fictive temperatures reached at the end of the cooling. During the heating, this small difference vanishes when the mean characteristic time of the system decreases down to an experimental value of a few seconds which depends on the heating rate. This means that, if one measures a static property, the volume for example, the difference in behavior between the two histories would then be roughly constant until the system melts. Apart from the extent of this difference, no clear link to the annealing temperature would be observed. In contrast, the measurement of a dynamic property, the dynamic modulus in our case, could reflect differences in the glassy relaxation during the heating, much before T_g is reached. Thus, in order to reproduce the simple memory effect within the TNM model, the dynamic modulus has to be calculated at each moment of the temperature cycle.

In order to keep a consistency between the non-exponentiality of the relaxation and the dynamic moduli, these last quantities are calculated using the same time distribution as the one used to account for the relaxation of the structure towards equilibrium—see the appendix for more details. Figure 8 shows an example of the moduli calculated, using the same temperature history as that of the experimental results of figure 4, and model parameter values reported in the literature [24]. Because of the chosen time distribution, the loss moduli in particular are rather different at low temperatures. However, the main differences between the two histories do not lie in this region.

In order to analyze the differences between the two thermal histories, the ratios $G'_{m-h}/G'_{\text{ref-h}}$ and $G''_{m-h}/G''_{\text{ref-h}}$ calculated during the heating are shown in figure 9 for

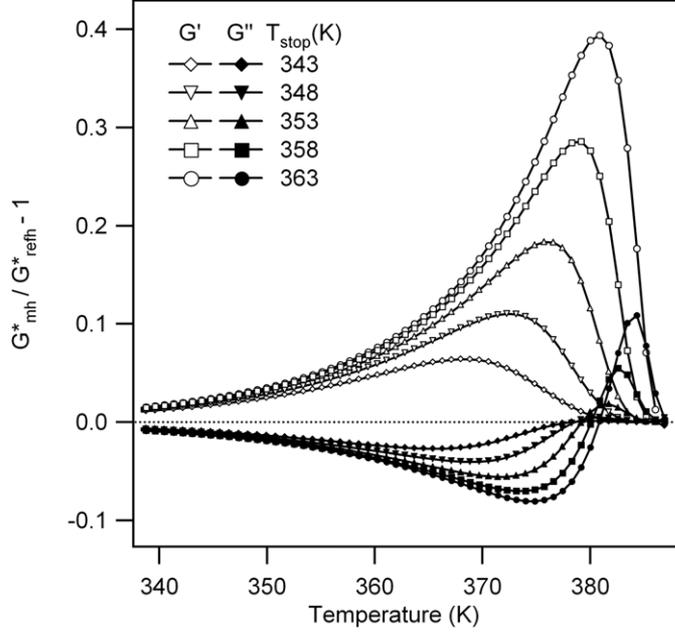


Figure 9. Ratios of the storage G'_{m-h}/G'_{ref-h} (open symbols) and of the loss G''_{m-h}/G''_{ref-h} (filled symbols) moduli calculated at 1 Hz during the heating ramp as a function of the temperature. The temperature rate is 0.083 K s^{-1} and the annealing step is set to 12 h at a temperature T_{stop} indicated on the figure.

different annealing temperatures, similarly as the experimental results of figure 6. For both quantities, a clear qualitative agreement is found. Both the position and intensity of the maximum of the storage moduli ratio (respectively the minimum of the loss moduli ratio) are an increasing function of the annealing temperature. Furthermore, the shapes of these curves are in good agreement and, within a few degrees, a quantitative agreement could be found. Since the moduli calculated after the TNM calculation are simplified in comparison to the experimental ones as explained above, a direct fit or a precise numerical agreement is meaningless (especially for the loss modulus). We have thus limited the use of this model to predict the variations of the position and intensity of the memory effect when varying the frequency, the annealing time and the cooling/heating rate. For all these parameters, a good qualitative agreement is found between the predictions of the model and the experimental observations (data not shown).

It is thus possible to conclude that the derivation of the TNM model used does account for the simple thermal memory effect. As a consequence, it could be stated that the main features of the model are sufficient to reproduce this memory effect. As detailed above, the two main assumptions are a wide distribution of the relaxation time and a very strong dependence of the characteristic time with temperature and structure. Since this last feature does not really need any discussion, we focus on the relevance of the characteristic time distribution for the memory effect. In the model, the width of the time distribution is given by the single β parameter of the KWW (Kahr–William–Watts) function used to describe the relaxation. The smaller β , the wider the distribution. In figure 10, the memory effect temperature $T_{max}^{G'}$ —the temperature at the maximum of position of

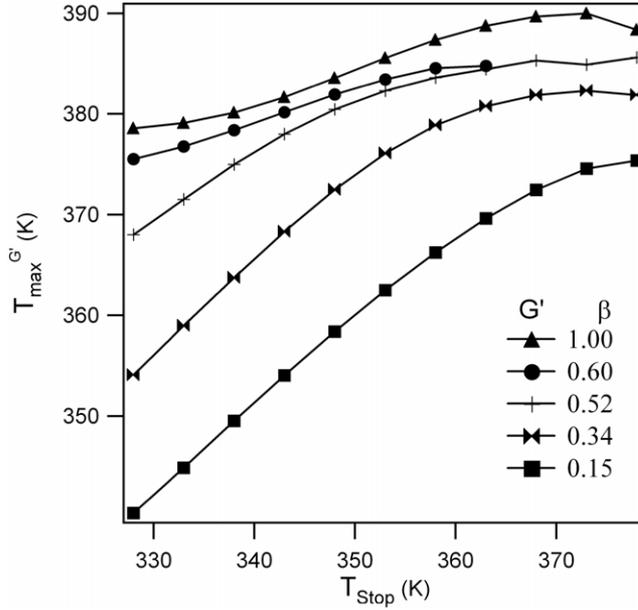


Figure 10. Temperature $T_{\max}^{G'}$ at which occurs the maximum of the ratio $G'_{m-h}/G'_{\text{ref-h}}$ as a function of the annealing temperature T_{stop} for different values of the β coefficient (see the appendix). The annealing time is 12 h, and the frequency ω_0 is 1 Hz. For $\beta = 0.6$, the last points could not be calculated because of the divergence of equation (A.8) when $\tau_0 > 1$ s. For $\beta = 1$, the distribution of the relaxation time (equation (A.7)) was replaced by a Dirac function centered at $\tau = \tau_0$. Note that the constant $\exp(A)$ of equation (A.3) has been normalized by the quantity $\Gamma(1/\beta)/\beta$, in order to ensure that the mean relaxation time $\langle \tau \rangle = \tau_0/\beta\Gamma(1/\beta)$ is kept constant while varying β .

$G'_{m-h}/G'_{\text{ref-h}}$ —is plotted as a function of the annealing temperature for different values of β . For high β values, i.e. thin time distributions, the position of the memory effect does not depend that much on the annealing temperature, whereas an almost linear relation (of slope 1) is found for the lowest values of β (large time distributions). Please note that, in order to obtain such a relation, it is necessary to have the same large distribution for the relaxation function and for the dynamic moduli; a dynamic modulus with one single time would not lead to this result, even with a non-exponential relaxation function.

It might thus be concluded that the memory effect is very closely linked to the heterogeneous dynamics of the glass.

We finally build from this conclusion to explain the memory effect with a simple physical argument. The wide time distribution could represent the coexistence of domains having heterogeneous dynamics [20, 23]. Each mode of relaxation has a given time of relaxation at a given temperature, and thus contributes to the dynamic mechanical response in a given range of temperature for a given frequency. When the system is cooled, the relaxation times of each mode become progressively slower and slower. As soon as they become smaller than the typical time of the experiment, the modes do not contribute any longer to relaxation. The modes which have been frozen at a given temperature will only contribute again to relaxation when the system is heated back to this temperature. While

the system is annealed at a temperature T_{stop} , the modes having a relaxation time smaller than t_{stop} can relax. These modes lie in the very short time part of the time distribution since the annealing is performed under T_g . When the system is reheated, the differences in the dynamic properties will vanish when the characteristic times of these particular modes become of the order of the experimental time; that appends a few degrees above T_{stop} . Thus, the measured property ratio between the non-annealed and the annealed system tends towards unity at this temperature. Since, at very low temperature, the dynamic property does not scan the modes that have been modified, the ratio also tends to unity at temperatures lower than T_{stop} . As a consequence, one deduces that this ratio should exhibit an extremum around T_{stop} . The sign of this extremum is then only linked to the sign of the local slope of the dynamic property versus time or temperature. The observation of a maximum for the storage modulus and a minimum for the loss modulus may thus only be a direct consequence of this argument.

The previous experiment enables us thus to detect small modifications of the shape of the relaxation spectrum easily. We will now use this property to detect how a small cyclic strain can modify the relaxation spectrum of a polymer glass.

3. Effect of the deformation on the physical aging memory

3.1. Experimental results

In this section, we will check how a cyclic mechanical excitation applied during the isothermal step influences the temperature dependence of the visco-elastic modulus. For that purpose, we will first characterize the modulus variations induced by a salvo of cyclic sinusoidal deformations applied during the annealing. We will thus compare the mechanical responses measured consecutively on the same sample using procedures 1 and 3.

First we analyze the effect of cyclic deformation of 1% amplitude applied during the whole annealing on the temperature dependence of the modulus.

Figures 11(a) and (b) compare the ratio of the real parts $[G'_m{}^{\gamma 1}/G'_{\text{ref}}]$ and of the imaginary parts $[G''_m{}^{\gamma 1}/G''_{\text{ref}}]$ of the shear moduli $G_m{}^{*\gamma 1}$ and G_{ref}^* measured applying procedures 3 and 1 respectively. In these figures, we see that the salvo of cyclic large deformation partly prevents the physical aging from developing during the isothermal step. The ratio of the real parts ($G'_m{}^{\gamma 1}/G'_{\text{ref}}$) seems to be more sensitive to the application of the cyclic mechanical stimulation than the ratio of the imaginary parts ($G''_m{}^{\gamma 1}/G''_{\text{ref}}$).

We see first that the modulus increases less during the annealing if cyclic deformations are applied: the system ages less when a mechanical stimulation is applied. The modulus $G_m{}^{*\gamma 1}$ remains perceptibly lower than G_m^* measured for temperature $T < T_{\text{stop}}$. During the heating ramp, the modulus $G_{m-h}{}^{*\gamma 1}$ is lower than G_{m-h}^* from T_1 to $380 \text{ K} = T_g - 17$ with T_g taken at the maximum of G''_{m-h} (see figure 2).

According to these experimental results, we concluded that the relaxation time spectrum of the glassy polymer is greatly changed by the mechanical stimulation. These modifications are less localized—in temperature—than the ones induced by simple annealing.

We now vary the amplitude γ_1 of the cyclic deformation applied during the isotherm. Figures 12(a) and (b) show the variation of the ratios $G'_{m-h}{}^{\gamma 1}/G'_{\text{ref-h}}$ and $G''_{m-h}{}^{\gamma 1}/G''_{\text{ref-h}}$

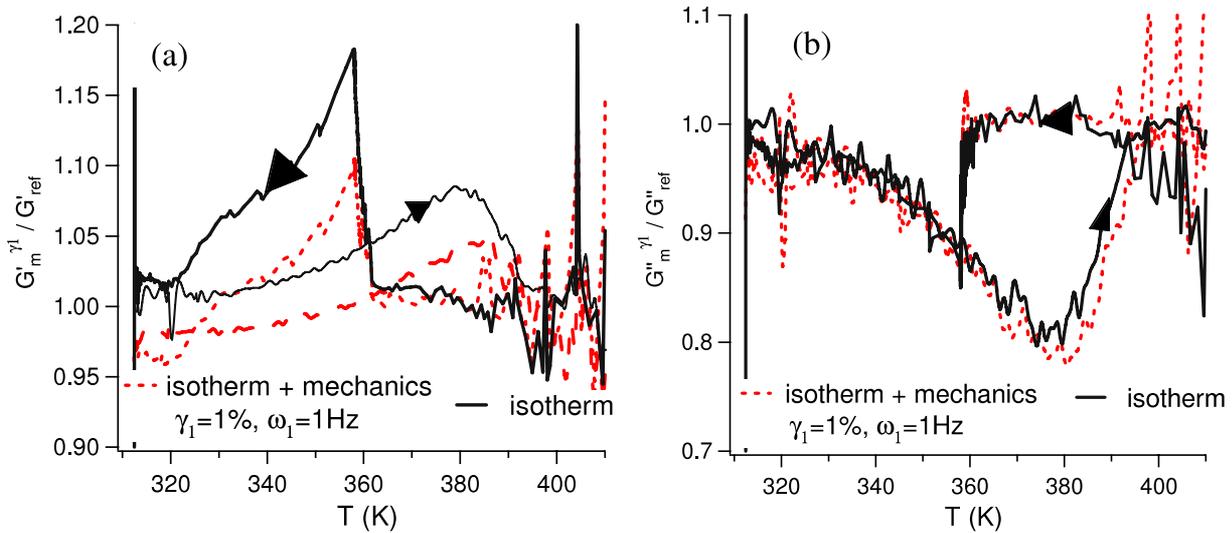


Figure 11. Temperature dependence of the ratios $G'_m{}^{\gamma_1}/G'_{ref}$ (a) and $G''_m{}^{\gamma_1}/G''_{ref}$ (b). The dashed lines represent data measured with the following experimental conditions: $dT/dt = 0.083 \text{ K s}^{-1}$, $\omega_0 = 1 \text{ Hz}$, $\gamma_0 = 0.07\%$, $T_{stop} = 358 \text{ K}$ and $t_{stop} = 7 \text{ h}$. The characteristics of the cyclic deformation salvo are $\gamma_1 = 1\%$, $\omega_1 = 1 \text{ Hz}$ and $t_{salvo} = t_{stop} = 7 \text{ h}$. The solid line corresponds to the temperature dependence of the ratios G'_m/G'_{ref} and G''_m/G''_{ref} observed applying a simple thermal history (procedure 2).

for increasing γ_1 measured during the heating ramp. We observe that, for increasing deformation amplitude:

- The ratio of the real part decreases. This elastic modulus lowering occurs over the whole temperature range and thus is not located on a restricted temperature window, as observed after a simple annealing.
- The minimum of the loss modulus ratio is shifted towards higher temperature. Its amplitudes slightly decreases.

In addition, we also studied the influence of the duration of a deformation salvo of 1% amplitude on the mechanical response measured during the heating ramp. The salvo of cyclic deformation was applied—for X h—at the end of an isothermal step of 8 h. The duration X of the cyclic salvo was varied from 0.5 to 4 h. Using this experimental condition, we observed that the duration of the cyclic deformation does not lead to significant variation in the experimental results presented in figures 11 and 12.

Lastly, we studied the influence of the mechanical stimulation frequency applied during the annealing. We compared the results obtained applying cyclic deformation of the same amplitude γ_1 , varying the frequency ω_1 from 0.1 to 10 Hz. The amplitude of the changes increases with the frequency ω_1 of the cyclic deformation salvo.

In conclusion to this experimental section, we observed that the mechanical stimulation modifies the visco-elastic response of the glassy polymer over the whole temperature range. However, the amplitude of the deviation induced by strain is maximum at a temperature slightly lower than $T_{max}^{G'}$ defined as the temperature where

Revealing the respective effect of aging and cyclic deformation through the memory effect in glassy polymers

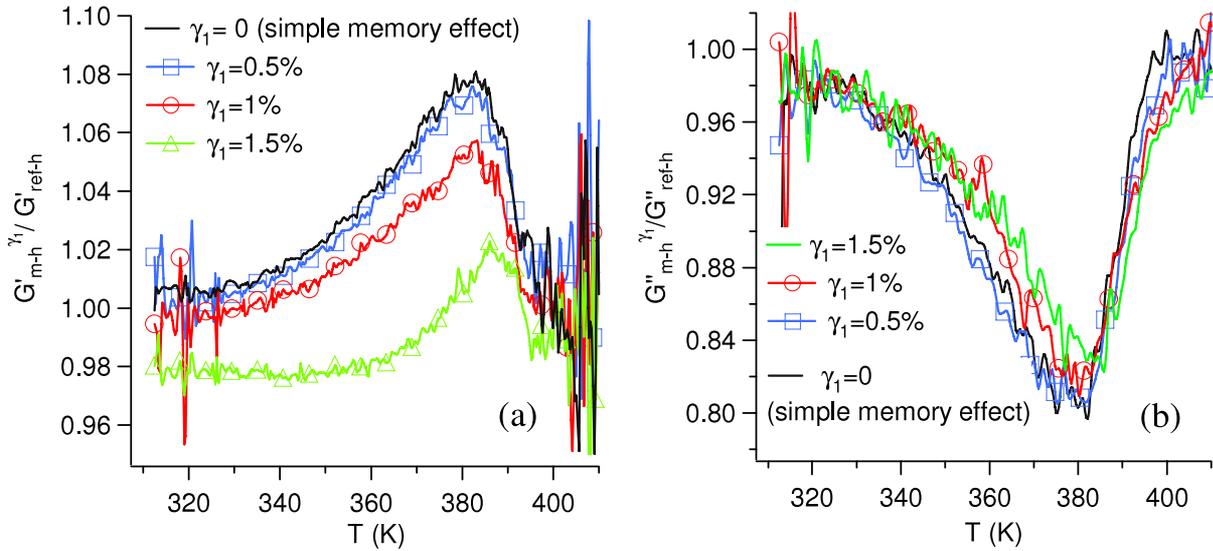


Figure 12. Dependence of (a) $G'_{m-h}^{\gamma_1}/G'_{ref-h}$ and (b) $G''_{m-h}^{\gamma_1}/G''_{ref-h}$ on the deformation amplitude γ_1 of the cyclic deformation salvo. Measurements were performed with the following conditions: $\gamma_0 = 0.07\%$, $\omega_0 = \omega_1 = 1$ Hz, $T_{stop} = 358$ K, $t_{salvo} = t_{stop} = 7$ h.

maximal physical aging was observed after a simple annealing. Moreover, the mechanical stimulus induces changes that are opposite in sign to the one observed for the simple memory effect.

4. Discussion: mechanical stimulus versus memory effect

If there is a huge literature on theoretical aspects of the dynamics of glasses, so far there are no satisfactory models for the plasticity of polymer glasses. Thus we focus only on straight experimental results—for plasticity—and the discussion below is meant to provide a physical picture of the observed phenomena.

We thus take advantage of this effect to investigate precisely how a mechanical stimulus applied in the glassy state changes the relaxation time spectrum. We thus submitted the sample to a mechanical stimulus during the annealing. We compared the contribution of the simple annealing to that of the mechanical stimulus (see figure 11).

We observed that the mechanical stimulus significantly modifies the memory effect for small deformation amplitude. We observed that a deformation amplitude of 1% is large enough to induce significantly large changes of the visco-elastic modulus of the polymer glass. 1% deformation amplitude is smaller than the plastic yield strain—about 5% in static condition.

Moreover, the effect on the elastic modulus of a salvo of sinusoidal deformation applied during annealing is opposite in sign to the one induced by a simple annealing. In figure 11(a) we can see that the elastic modulus is decreased by mechanical stimulus. In order to identify the temperature distribution of the mechanical stimulus, we separated the contribution of the annealing from that due to the cyclic deformation salvo. For that purpose, we have compared the visco-elastic response measured with ($G_m^{*\gamma_1}$ from procedure

Revealing the respective effect of aging and cyclic deformation through the memory effect in glassy polymers

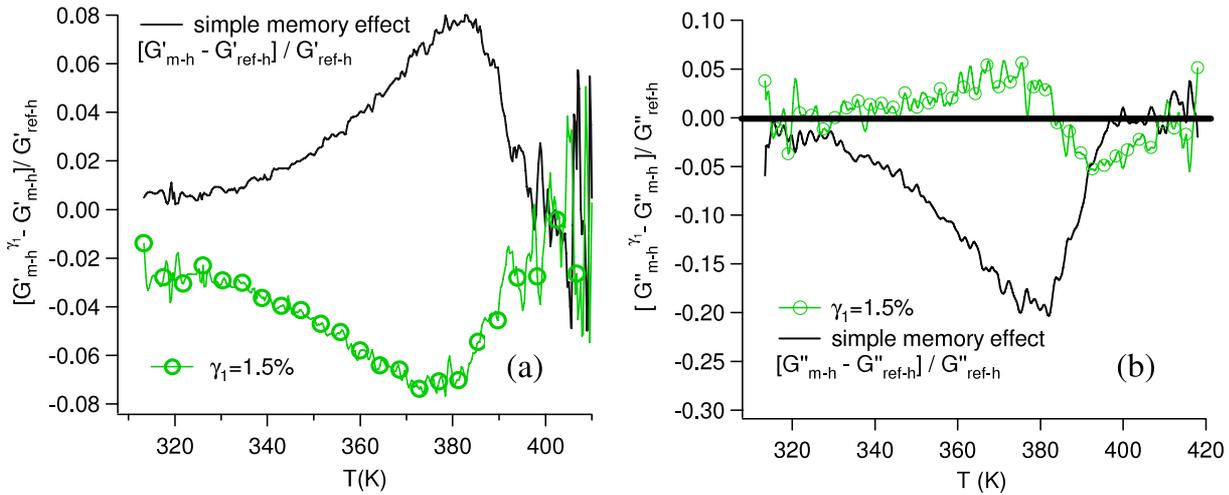


Figure 13. Comparison of the contribution of annealing (solid line) and the contribution of cyclic deformations (circles) on the real part (a) and the imaginary part (b) of the shear modulus of PMMA chains.

3) and without (G_m^* from procedure 2) a mechanical stimulus during the annealing. Figure 13(a) shows the temperature dependence measured during the heating ramp of the two quantities $(G'_{m-h} - G'_{ref-h}) / G'_{ref-h}$ and $(G_{m-h}^{\gamma_1} - G'_{m-h}) / G'_{ref-h}$. $(G'_{m-h} - G'_{ref-h}) / G'_{ref-h}$ corresponds to the elastic modulus difference between the unannealed sample G'_{ref-h} (procedure 1) and the annealed one G'_{m-h} (procedure 2) normalized by the elastic modulus of the unannealed sample G'_{ref-h} . This quantity represents the contribution of the annealing to the time relaxation spectrum of the glassy system and is plotted with solid lines. We plotted with circles the contribution of the mechanical stimulus $(G_{m-h}^{\gamma_1} - G'_{m-h}) / G'_{ref-h}$, that is the normalized elastic modulus deviation between the simply annealed sample G'_{m-h} (procedure 2) and the one annealed with mechanical stimulus $G_{m-h}^{\gamma_1}$ (procedure 3). In figure 13(a), we see clearly that if the effect of mechanics is opposite in sign to the one of annealing, it is also wider and extends towards very low temperature.

We can also discuss similarly, but in a more complex way, the effect on the loss modulus of a mechanical stimulus applied during the annealing. On figure 13(b), we observe that $(G_{m-h}^{\gamma_1} - G''_{m-h}) / G''_{ref-h}$ is positive at low temperature and become negative at temperatures higher than $T_{min}^{G''}$. Let us recall that, for simple annealing, a change of sign is also predicted by the TNM model (see figure 9), and is due to the fact that the derivative of the loss modulus with temperature changes in this domain. Thus, because the loss modulus depends only slightly on temperature in the vicinity of its maximum, any modification of the time relaxation spectrum would have a small effect on the loss modulus over this temperature range. In contrast, as the elastic modulus exhibits a significant and monotonic variation with temperature, it is quite sensitive to any modification of the time relaxation spectrum. However, from the effect of mechanical stimulus on both the elastic modulus and the loss modulus, we can conclude that the effect of a cyclic strain—as compared to that of annealing—has an opposite sign, and affects a wider range of the time spectrum. This is qualitatively consistent with the SGR model, for which the

mechanics has a wider impact than temperature on the relaxation time spectrum [2]. Our experiments show that a cyclic strain would be less selective in terms of the various modes of relaxation of the system. In order to gain insight into this phenomenon, one would need to work on possible modification of the TNM model that could include mechanics, as TNM is the only present model that satisfactorily describes the effect of simple annealing. This difficult task is beyond the scope of this paper.

5. Conclusion

We have measured the respective effects of annealing at rest and under cyclic strain, on the visco-elastic modulus of a glassy polymer.

We show that simple annealing reveals a so-called ‘memory effect’ that can be simply described by the TNM model. It reveals mainly that the relaxation spectrum is very wide, and evolves according to the thermal history in a quite simple way. In fact this effect allows us to detect precisely the time evolution of the relaxation spectrum at a given temperature. So we use this phenomenon to analyze the effect of cyclic strain on the relaxation spectrum. We show that a cyclic strain larger than 0.5% modifies the relaxation spectrum in a significant way. This modification has a sign opposite to that of thermal annealing and affects a wider part of the spectrum.

Appendix

In order to account for the simple memory effect, the Tool–Narayanaswamy formalism is used. In such a simple model of the glassy state, the system evolves towards equilibrium, according to a mean relaxation time that depends on both the temperature and the actual state. The departure from equilibrium is given by the difference between the temperature T and the Tool fictive temperature T_f [25]. The following set of equations allows us to calculate the evolution of T_f after a temperature step from T towards $T + \Delta T$. If $T_f = 0$ at time $t = 0$, $T_f(t)$ is given by

$$T_f(t) = T + \Delta T \left(1 - e^{-\tilde{t}^\beta}\right), \quad (\text{A.1})$$

where β is the exponent of the KWW function. \tilde{t} is a reduced time, defined as

$$\tilde{t} = \int_0^t \frac{dt'}{\tau_0 [T(t'), T_f(t')]} \quad (\text{A.2})$$

Within this formalism, the fictive temperature evolves towards equilibrium with its own dynamics, assumed to be proportional to a characteristic time τ_0 . Equation (A.2) requires an estimation of the characteristic time as a function of T_f and T . We used for this characteristic time the Adam–Gibbs–Fulcher formulation given by

$$\tau_0 [T(t'), T_f(t')] = \exp \left(A + \frac{B}{T(1 - T_0/T_f)} \right), \quad (\text{A.3})$$

where B , A and T_0 are related to the William–Landel–Ferry parameters, many times reported in the literature.

The evolution of the fictive temperature in the case of an arbitrary thermal history may be obtained by the use of the Boltzmann superposition principle. The following

Table A.1. PMMA Adams–Gibbs–Fulcher parameters used in the calculations.

A	B (K)	T_0 (K)	β
-55.45	3430	325	0.34

expression was used to compute the fictive temperature for the different thermal history of figure 1, starting at $t = 0$ at equilibrium:

$$T_f(t) = T(0) + \int_0^t dt' \frac{dT}{dt'} \left[1 - \exp \left(- \left\{ \int_{t'}^t \frac{dt''}{\tau_0 [T(t''), T_f(t'')]} \right\}^\beta \right) \right]. \quad (\text{A.4})$$

Then, one has to relate the evolution of T_f to an observable property. In this study, the complex modulus at a given frequency was measured. In order to compare the results of the model with the experimental ones, a complex modulus is calculated starting from a given time spectrum $\rho(\tau)$ according to the expression [26]

$$G^*(\omega, \tau_0) = \int_0^{+\infty} \frac{\omega\tau(\omega\tau + i)}{1 + \omega^2\tau^2} \rho(\tau) d\tau. \quad (\text{A.5})$$

In order to keep a consistency between the observable property and the relaxation, the time distribution used in equation (A.5) is that of the KWW function used for the relaxation function $\phi(t)$, so that

$$\phi(t) = \int_0^{+\infty} \rho(\tau) e^{1/\tau} d\tau. \quad (\text{A.6})$$

Lindsey and Patterson [27] developed an analytical expression for the distribution function corresponding to the KWW relaxation function. $\rho(t)$ is given by

$$\rho(\tau) = -\frac{\tau_0}{\pi\tau^2} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sin(\pi\beta k) \Gamma(\beta k + 1) \left(\frac{\tau}{\tau_0} \right)^{\beta k + 1}. \quad (\text{A.7})$$

Equations (A.1), (A.2), (A.5) and (A.7) form a complete set that allows us to determine the complex modulus at all time of any thermal history. Inserting equation (A.7) into equation (A.5) leads to a simple integration over τ and allows us to calculate the dynamic moduli as the series

$$G'(\omega\tau_0) = 1 + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \cos\left(\frac{\pi\beta k}{2}\right) \Gamma(\beta k + 1) (\omega\tau_0)^{-\beta k}, \quad (\text{A.8a})$$

$$G''(\omega\tau_0) = -\sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \sin\left(\frac{\pi\beta k}{2}\right) \Gamma(\beta k + 1) (\omega\tau_0)^{-\beta k}, \quad (\text{A.8b})$$

which converges rapidly when $\omega > 1/\tau_0$. The parameters used for the calculation are those reported in the literature for PMMA [24], and are given in table A.1.

This calculation was applied systematically on a reference cycle and a cycle where a pause in the cooling was applied at T_{stop} for t_{stop} . These cycles are exactly those used for the experiment.

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