

**The segmental  $\alpha$ -relaxation for the first-step and the sub-Rouse modes for  
the second-step in enthalpy recovery in the glassy state of polystyrene**

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**Abstract**

Cangialosi and coworkers found two steps in the enthalpy recovery deep in the glassy state of high and low molecular weight bulk polystyrene(PS). We attribute the first step to the segmental  $\alpha$ -relaxation and the second step to the sub-Rouse modes, and explain the observed two-step enthalpy recovery by the dynamic properties of the two processes in bulk PS in the framework of the Coupling Model (CM). The two-step enthalpy recovery also was found recently in nanometer thin films of polystyrene (PS). On decreasing film thickness, the first step was shifted to much lower temperature than the second step, and the effect is explained by the segmental  $\alpha$ -relaxation shifting to lower temperature on decreasing film thickness much more than the sub-Rouse modes, which is predicted by the CM. Furthermore, the dependences of the faster and slower processes of the two-step enthalpy relaxation on film thickness are exact analogues of two effects observed on decreasing the thickness  $h$  of freestanding polystyrene films. One effect is the observation of two transitions by ellipsometry. There we associated the lower transition at  $T_g^l(h)$  with the segmental  $\alpha$ -relaxation and the upper transition at  $T_g^u(h)$  with the sub-Rouse modes, and successfully explained the experimentally observation of  $T_g^l(h)$  decreasing more rapidly than  $T_g^u(h)$  on

decreasing  $h$  also by the CM. The other effect is the rubbery stiffening observed by creep compliance measurements on decreasing  $h$  of freestanding films in many polymers including PS. This effect was satisfactorily explained by the additive contributions to compliance from the sub-Rouse modes and the segmental  $\alpha$ -relaxation, and the more rapid decrease of the segmental  $\alpha$ -relaxation time  $\tau_\alpha(T,h)$  with decreasing  $h$  than the sub-Rouse relaxation time  $\tau_{sR}(T,h)$ , again using the CM. These two analogues of the two-step enthalpy recovery in bulk and nanometer PS thin films strengthen the common CM explanation of the first step by the segmental  $\alpha$ -relaxation and the second step by the sub-Rouse modes.

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## 1. Introduction

Starting in 2011 Cangialosi and coworkers<sup>1,2</sup> studied the kinetics of enthalpy recovery of three polystyrene samples with different molecular weights at temperatures significantly below the nominal glass transition temperature ( $T_g$ ) by physical aging for aging times up to one year. In a 2013 publication<sup>2</sup>, they showed this intermediate aging plateau separates two relaxation mechanisms, one faster and the other slower, in high and low molecular-weight polystyrene and polycarbonate. This two-step process of enthalpy recovery with an intermediate plateau is a novel finding and interesting, but is at odds with the monotonic decrease of departure from equilibrium with increasing logarithm of aging time  $t_a$  to reach equilibrium observed by Kovacs in his classical volume recovery experiments<sup>3</sup>, and in the volume and enthalpy recovery studies of others<sup>3-10</sup>, and also with the current theories of structural relaxation that involve only one characteristic rate or change in the relaxation time with the fictive temperature and time. The existence of intermediate

aging plateau led Koh and Simon<sup>11</sup> to make in 2013 their independent study enthalpy recovery at an aging temperature 15 °C below the nominal  $T_g$ , for aging times up to 1 year, on a bulk polystyrene sample with number-average molecular weight of 92 800 g/mol and a weight-average molecular weight of 221 000 g/mol. The intermediate plateau was not found, and the results indicate that the equilibrium liquid enthalpy line can indeed be reached for aging at 15 K below  $T_g$ . Thus a controversy was created but there was no resolution since Cangialosi and coworkers maintained their findings in several reviews, the last one was in 2016.<sup>12,13,14</sup> However, the controversy may not be real because the experimental conditions in the studies of the two groups are different. For example, Cangialosi et al. used a monodisperse high molecular weight PS, while Koh and Simon used a polydisperse one. The differences in the samples and other experimental conditions may be the cause of not observing the same result.

On the other hand, Simon and coworkers<sup>15,16</sup> reported the study of the structural recovery of a film of monodisperse polystyrene ( $M_n = 1,998,000$  g/mol, PDI =1.02) at aging temperatures from 50.5 to 100.5 °C using flash DSC for a high fictive temperature glass obtained after cooling at 1000 K/s. The departure from equilibrium decreases smoothly and approximately linearly with logarithmic aging time without any evidence of intermediate plateau. However the aging time scale accessed<sup>15,16</sup> is less than  $10^5$  s, which could be too short to reach the first plateau and to observe the second decay, and the reason of the difference from the results of Cangialosi and coworkers.

The impasse for resolving the controversy may be mitigated by considering new result from the study of enthalpy recovery in stacked glassy polystyrene (PS) films with thickness from 30 to 95 nm over a wide temperature range below  $T_g$ ,<sup>17,18</sup> and in polystyrene (PS) nanospheres<sup>19</sup>. It was shown that the time evolution toward equilibrium is composed of two steps<sup>17,18</sup>, analogous to bulk PS. In comparison to bulk PS, the time scales of the two relaxations of recovery are

considerably shorter and decreasing with the film thickness. The fast process, allowing partial enthalpy recovery toward equilibrium, displays Arrhenius temperature dependence with low activation energy, whereas the slow process follows pronounced super-Arrhenius temperature dependence. Moreover, the fact that the fast process was found to be effective in inducing significant densification at temperatures far below  $T_g$  is interesting and revealing.

In this paper we make good use of the results of enthalpy recovery in the nanometer thin PS films<sup>17,18</sup>, nanospheres<sup>19</sup>, and bulk PS<sup>2</sup> to identify the two molecular mechanisms for the fast and the slow processes therein theoretically in the framework of the Coupling Model (CM)<sup>20</sup> specialized to polymer viscoelasticity<sup>21,22,23,24,25,26,27,28</sup>. We show the fast process comes from the segmental  $\alpha$ -relaxation well known to be responsible for glass transition, while the slow process originates from the sub-Rouse modes,<sup>21,22,23,24,25,26,27,28,29</sup> which is slower than the segmental  $\alpha$ -relaxation, but faster than the better known entropic Rouse modes. Thus naturally the sub-Rouse modes constitute the viscoelastic mechanism to account for the slower decay in the two-step enthalpy recovery, since the faster decay is generally agreed to come from the segmental  $\alpha$ -relaxation,

In this paper, we consider the experimental results of Cangialosi and coworkers and provide the two mechanisms for the two-step enthalpy relaxation in bulk and nanometer thin films of PS. Notwithstanding, some of the works carried out in the past by others may not be at odds with the two-step decays because the experiments were carried out for times too short, or not enough far below  $T_g$  (for instance in ref.10), where at best one can see the first decay. Moreover, the work of Andreozzi and co-workers<sup>6</sup> and other authors showed that a plateau with partial enthalpy recovery is attained in the experiments, compatible with the existence of a second decay

at longer times. Also the analysis of data by Hutchinson and Kumar<sup>7</sup> shows at the lowest aging temperatures investigated the partial enthalpy recovery to a plateau is attained.

## **2. The segmental $\alpha$ -relaxation and the sub-Rouse modes for the 2-step enthalpy recovery**

The sub-Rouse modes in polymers were first revealed by combined creep compliance and stress relaxation experiment, and by light scattering experiments on polyisobutylene in 1995.<sup>21,22,23</sup> Since then, the general existence of the sub-Rouse modes in other polymers has been confirmed and their properties brought out by various experimental studies<sup>24,25,26,27,28,29</sup>. In this section we invoke the properties of the sub-Rouse modes supported theoretically by the Coupling Model (CM) to justify that they are responsible for the slower process in the two-step enthalpy recovery observed by Cangialosi and coworkers<sup>1,2,17,18,19</sup>. Deduced from experiments, these properties of the sub-Rouse modes as well as the theoretical justifications from the CM have been well documented in publications in archival journals. Therefore we just state these properties, but do not duplicate the details and theoretical rationalization involved to arrive at each of these properties. Nevertheless, references are given following the cited property for anyone interested to retrieve the details.

We start with the existence of the sub-Rouse modes in bulk polymers in general including polystyrene of high<sup>21,21,22,25,26,27,28,29,30</sup> and low molecular weights<sup>24</sup> was demonstrated before by experiments. Their contribution to the creep compliance is known and delineated from that of the segmental  $\alpha$ -relaxation and Rouse modes<sup>30,31,32</sup>. The sub-Rouse modes shift to longer times on elevating pressure like the segmental  $\alpha$ -relaxation.<sup>33,34,35,36,37,38,39</sup> The activation volumes for the two processes are very similar, and their relaxation times,  $\tau_{sR}$  and  $\tau_{\alpha}$ , are functions of the combined variable,  $T/\rho^{\gamma}$ , with the same  $\gamma$  where  $\rho$  is the density. Thus like the segmental  $\alpha$ -relaxation, the

sub-Rouse modes are coupled to density and respond to physical aging<sup>40,41</sup>. Heat capacity spectroscopy from the  $3\omega$  method was applied to measure the product of thermal conductivity  $\kappa$ , density  $\rho$ , and heat capacity  $C_p$ , and the frequency dispersion was assumed to come only from  $C_p^*(\omega, T) = C_p'(\omega, T) - iC_p''(\omega, T)$ .<sup>42,43</sup> The isochronal data of  $C_p''(\omega, T)$  of PS show not only the prominent loss peak contributed by the segmental  $\alpha$ -relaxation but also an excess loss at high temperatures.<sup>42,43</sup> The latter is possibly the contribution from the sub-Rouse modes, and thus the enthalpic nature of the sub-Rouse modes is revealed by heat capacity spectroscopy. One should not directly compare the sizes of the responses from segmental  $\alpha$ -relaxation and sub-Rouse modes from linear response measurements, as those in the specific heat capacity measurements in refs.42 and 43 at 1 Hz to 1 kHz where only the reversing specific heat is recorded, with those carried out in the non-linear regime of enthalpy recovery experiment at much longer times. In the latter, the magnitude of the enthalpy recovered is the non-reversing specific heat and the total specific heat.

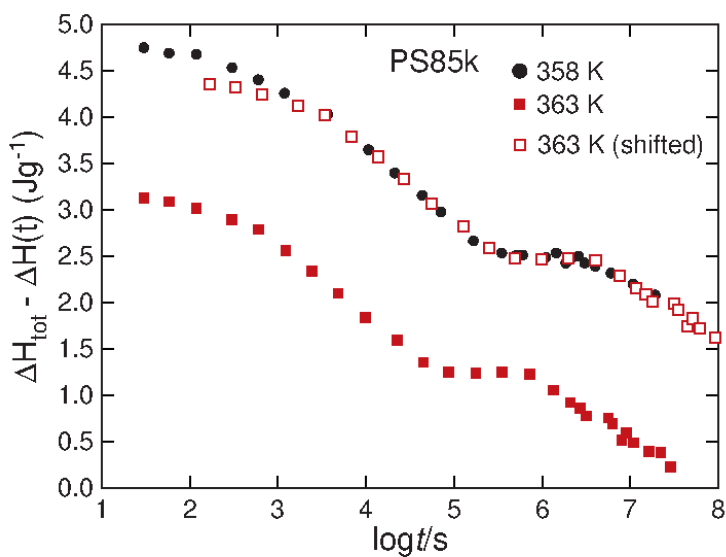
## 2.1 Enthalpy recovery in bulk PS

It is generally agreed experimentally and theoretically that the segmental  $\alpha$ -relaxation makes contribution to enthalpy relaxation and recovery and volume<sup>3</sup>. Therefore, the segmental  $\alpha$ -relaxation should be the more prominent one of the two relaxations in the 2-step enthalpy recovery of PS. Likely it is the mechanism responsible for the faster process observed to have the larger enthalpy recovered. The nature of the slower process had not been identified before by Cangialosi and coworkers<sup>1,2,17,18,19</sup>. We suggest that it originates from the sub-Rouse modes, which are slower than the segmental  $\alpha$ -relaxation, and their relaxation times  $\tau_{sR}$  are coupled to density. Our suggestion would have a problem if we accept totally the equilibration times  $\tau_{eq,1}$  and  $\tau_{eq,2}$  claimed

by Cangialosi et al.<sup>2,17</sup> to correspond to the first and the second plateaus, and identify them with  $\tau_\alpha$  and  $\tau_{sR}$  respectively. This is because the  $\tau_{eq,2}$  in their<sup>2</sup> Fig.3 has the Vogel-Fulcher-Tammann (VFT) temperature dependence much stronger than the approximately Arrhenius temperature dependence of  $\tau_{eq,1}$ , but instead we know that  $\tau_{sR}$  has weaker temperature dependence than  $\tau_\alpha$ .<sup>21,22,23,24,25,26,29,30,31,32,33,34,35,36,37,38,39,40,41,44</sup> However, upon closer examination of the time evolution of the recovered enthalpy at different temperatures for the high molecular weight polystyrene with  $M_n=85$  kg/mol (PS85k), the presence of second plateau in their<sup>2</sup> figure 2a at 363 K and 358 K used to obtain  $\tau_{eq,2}$  and deduce its VFT dependence is not evident, and therefore may not be used to deduce that  $\tau_{eq,2}$  has the strong VFT temperature dependence below  $T_g$ . To show this, we have reproduced the data at the two lowest temperatures 363 K and 358 K in Fig.1, and shift the data at 363 K to coalesce its first plateau with that of the data at 358 K. The enthalpy recovery data for the low molecular weight PS with  $M_n=7$  kg/mol (PS7k) are presented in Fig.2, together with the data 356 K shifted to coalesce with the data at 353 K in same manner as in Fig.1. The overlap of the shifted 363 K data with the 358 K data in Fig.1 and the overlap of the shifted 356 K data with the 353 K data in Fig.2 at times past the first plateau suggests the changes of the equilibration times of the faster and slower enthalpy recovery processes with the change in temperature are not too different and are not diverging at lower temperatures, in contrast to that suggested in Fig.3 in ref.2. With this modification of the temperature dependence of  $\tau_{eq,2}$ , the data of Cangialosi and coworkers are consistent with the known relation between the temperature dependences of  $\tau_\alpha$  and  $\tau_{sR}$  as well as our identification of the faster and slower processes as the segmental  $\alpha$ -relaxation and the sub-Rouse modes respectively.

Despite the consistency of our explanation with the two-step enthalpy recovery data in bulk PS, it is not sufficient for the verification, and more evidences are needed to complete the proof.

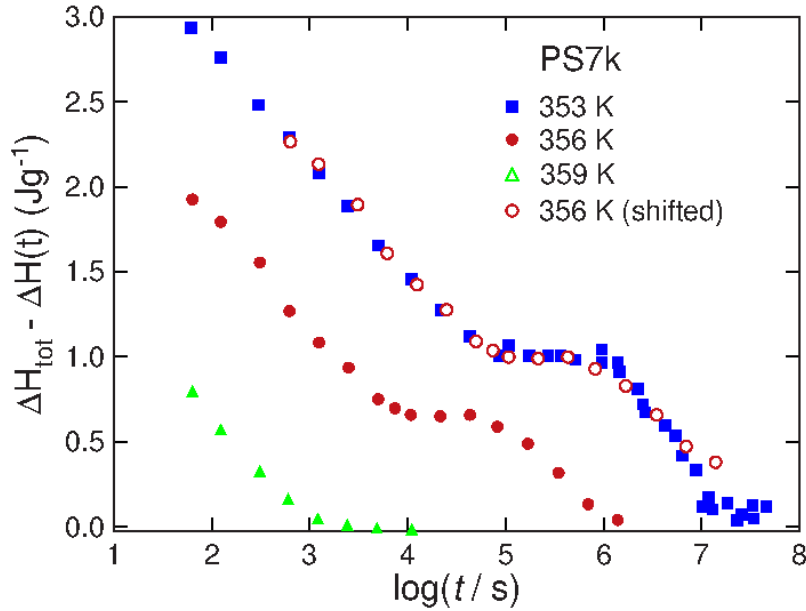
These evidences are provided in the following section by the drastic changes of the two-step enthalpy recovery in nanometer PS thin films on decreasing the film thickness. The proof comes from the fact that these drastic changes in nanoconfinement are explainable by the corresponding changes of segmental  $\alpha$ -relaxation and the sub-Rouse modes as predicted by the CM<sup>31,32,40,41</sup>. Further support comes from two effects in nanometer PS thin films that are analogues of the two-step enthalpy recovery, and have been successful explained by the segmental  $\alpha$ -relaxation and the sub-Rouse modes. One effect is the observation of two transitions by ellipsometry in freestanding nanometer PS thin films, and the other is the rubbery stiffening observed by creep compliance measurements on decreasing the thickness of freestanding films of many polymers including PS. These two effects and the explanations by the CM are discussed in the following section in conjunction with our current explanation of the two-step enthalpy recovery experimental data.



**Figure 1.** Time evolution of the recovered enthalpy at 363 and 358 K for PS85k. Additionally, the data at 363 K have been shifted horizontally and vertically to coalesce its first plateau with that of the data at 358 K. The purpose of superposing the two sets of data is to show the temperature



dependences of the equilibration times of the faster and slower enthalpy recovery processes are not very different and not diverging at lower temperatures, in contrast to that suggested in Fig.3 in ref.2.



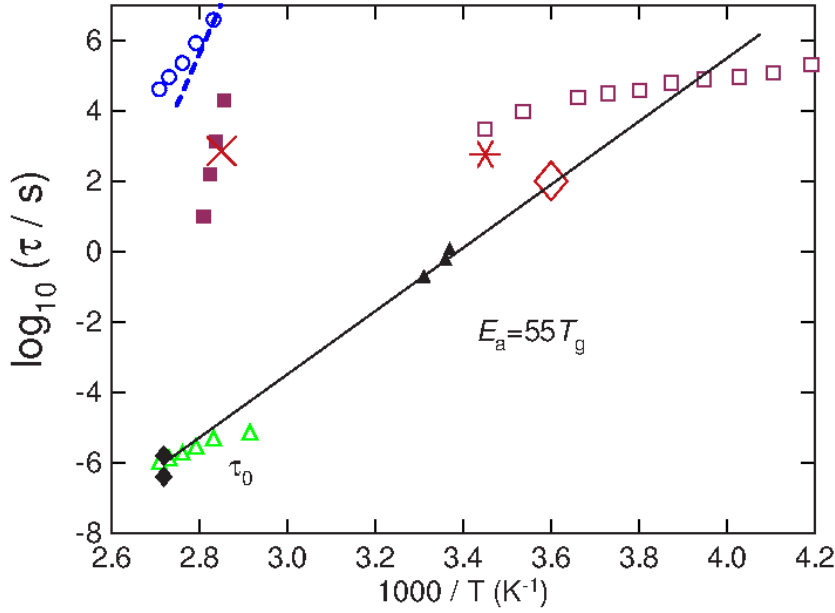
**Figure 2.** Time evolution of the recovered enthalpy at three temperatures for PS7k. Additionally, the data at 356 K have been shifted horizontally and vertically to coalesce its first plateau with that of the data at 353 K.

## 2.2 Nanometer thin PS films

Based on the Coupling Model (CM) and the argument of the coupling parameter  $n_\alpha$  of segmental  $\alpha$ -relaxation is larger than  $n_{sR}$  of the sub-Rouse modes, we have explained the weaker temperature, pressure, and  $TV^\gamma$  dependences of the latter than the former<sup>24,25,30,31,32,33,37,38,39,40</sup>. By

the same reasoning, the reduction of the  $\alpha$ -relaxation time  $\tau_\alpha$  on decreasing the thickness of freestanding polymer thin films is much more than that of the sub-Rouse (sR) relaxation times  $\tau_{sR}$ .<sup>31</sup> This result derived from the CM leads to larger difference between  $\tau_{sR}$  and  $\tau_\alpha$  or increased separation of the  $\alpha$ -relaxation from the sub-Rouse modes, and the difference/separation respectively increases with decreasing film thickness<sup>31</sup>. The resultant effect was observed experimentally in creep compliance measurements by the rubbery-like stiffening behaviors for many polymer thin films by McKenna and coworkers<sup>45-51</sup>, and others<sup>52</sup>. The CM explanation of the effect was bolstered by the strong correlation of the rubbery stiffening index with  $n_\alpha$  found when considering the results from 8 different polymers including PS, PC, and PIB.

This effect found by McKenna and coworkers in creep compliance of nanometer thin polymer films, and explanation by the CM is relevant to our explanation of the two-step enthalpy recovery of Cangialosi and coworkers. This can be inferred from the similarly much larger decrease of the enthalpy equilibration time  $\tau_{eq,1}$  of the faster ( $\alpha$ ) process than  $\tau_{eq,2}$  of the slower (sR) process with decrease of PS films thickness down to 30 nm observed by Boucher et al.<sup>17,18</sup>. The trend can be seen from Fig.4 of Boucher et al.<sup>17</sup>, where the increasing separation of the logarithm of the equilibration times of the first and the second decays with decreasing thickness is evident by inspection of the data of bulk, 95 nm, 67 nm and 30 nm PS films. We have taken from this figure the two equilibration times  $\tau_{eq,1}$  (open squares) and  $\tau_{eq,2}$  (closed squares) of the 30 nm thin film and the  $\tau_{eq,1}$  (open blue circles) of bulk PS, and reproduce them in our Fig.3.



**Figure 3.** The equilibration times  $\tau_{eq,1}$  and  $\tau_{eq,2}$  of the 30 nm thin film (purple open and closed squares respectively), and  $\tau_{eq,1}$  of bulk PS (open blue circles) from Boucher et al.<sup>17</sup>. The segmental relaxation time,  $\tau_{\alpha}(T)$ , measured by PCS on a 22 nm freestanding PS film (black filled triangles)<sup>60</sup>. The large red diamond and red star with coordinates  $(1000/T_g^l(h), 2.76)$  where  $T_g^l(h)$  is the lower transition temperature from ellipsometry measurements<sup>53</sup> for film thickness that is approximately the same as  $h=22$  and 33 nm respectively<sup>40,41</sup>. The red multiplication sign with coordinates  $(1000/T_g^u(h), 2.85)$ , where  $T_g^u(h)$  is the upper transition temperature from ellipsometry measurements for film thickness approximately the same as  $h=33$  nm.<sup>53</sup> The two black filled diamonds are the primitive relaxation times  $\tau_0$  of bulk PS at  $T_g$  calculated by the CM equation with  $n_{\alpha}$ . The solid black line is supposed to be an estimate of  $\tau_0$  of bulk PS for  $T \leq T_g$ . The broken blue line on top is  $\tau_{\alpha}(T)$  of bulk PS calculated by the CM equation. The green triangles are  $\tau_0$  of bulk PS calculated from  $\tau_{eq,1}$  of bulk PS (open blue circles).

Ellipsometry measurements of freestanding high molecular weight polystyrene (PS) films with thickness less than 70 nm showed the presence of two glass transitions originating from two distinctly different and simultaneous mechanisms to reduce the glass transition temperature<sup>53</sup>. The lower transition at temperature  $T_g^l(h)$  is the same as found before in freestanding PS films by others<sup>54,55,56</sup>, and can be explained by the large enhancement of mobility of the segmental  $\alpha$ -relaxation due to the free surfaces, finite size effects,<sup>57</sup> and induced orientations of the PS chains<sup>58</sup>. The upper transition at a higher temperature  $T_g^u(h)$  is novel.<sup>53</sup> The two transitions cannot be explained by segmental  $\alpha$ -relaxation alone simply by occurrence at two different locations of the film as discussed in <sup>32,40,41</sup>. This is because this hypothesis implies the difference,  $T_g^u(h) - T_g^l(h)$ , would decrease as film thickness decreases, which is opposite to the increase observed experimentally<sup>53</sup>. Therefore, the upper transition must come from another viscoelastic mechanism other than the segmental  $\alpha$ -relaxation of PS. The sub-Rouse modes have been suggested to give rise to the upper transition and the suggestion was justified from the properties of these modes<sup>32,40,41</sup>. Physical aging was observed at a temperature below the upper transition, but above the lower transition.<sup>59</sup> This result was interpreted as indicative of the upper transition being an actual glass transition associated with the  $\alpha$ -relaxation<sup>59</sup>, and not the sub-Rouse modes<sup>32,40,41</sup>. Such an interpretation was based on lack of knowledge about the properties of the sub-Rouse modes, and it has been debunked in ref.<sup>40</sup> after presenting evidences that the sub-Rouse modes do respond to physical aging. Anyhow, if according to the interpretation of the authors of ref.<sup>59</sup> that both the upper and lower transitions are actual glass transition associated with the  $\alpha$ -relaxation, the difference,  $T_g^u(h) - T_g^l(h)$ , should decrease as the two  $\alpha$ -relaxations tend to merge together as the film thickness decreases. This is opposite to the increase of the difference, which was observed experimentally<sup>53</sup>. After having correctly identified the upper transition with the sub-Rouse modes,

the observation of physical aging at a temperature below the upper transition, but above the lower transition<sup>58</sup> is a direct proof of the sub-Rouse modes do age with time. The two transitions in the 33 nm freestanding PS films with  $M_n=820,000$  g/mol from study by ellipsometry<sup>53</sup> are analogous to the two processes in stacked 30 nm PS freestanding films from enthalpy recovery<sup>17,18</sup>. Therefore it is natural to compare the enthalpy equilibration times  $\tau_{eq,1}(T)$  and  $\tau_{eq,2}(T)$  of the 30 nm thin film with  $\tau_\alpha(T)$  and  $\tau_{sR}(T)$  both assumed equal to 100 s at  $T_g^l(h)$  and  $T_g^u(h)$  respectively of the  $h=33$  nm freestanding film from ellipsometry<sup>53</sup>. The values of  $T_g^u(h)$  and  $T_g^l(h)$  for  $h=33$  nm were deduced from the ellipsometry data before<sup>40,41</sup>, and the coordinates  $(1000/T_g^l, 2.76)$  and  $(1000/T_g^u, 2.85)$  for  $\log \tau_\alpha(T_g^l)$  and  $\log \tau_{sR}(T_g^u)$  respectively of the 33 nm film are entered into the relaxation map of Fig.3 as the cross and the star respectively. As can be seen by inspection, the value of  $\tau_{eq,1}(T)$  at  $T=T_g^l=290$  K is about one order of magnitude longer than  $\tau_\alpha(T_g^l)$ , and the same is true for  $\tau_{eq,2}(T)$  at  $T=T_g^u=350$  K compared with  $\tau_{sR}(T_g^u)$ . The values of  $\tau_\alpha(T_g^l)$  and  $\tau_{sR}(T_g^u)$  in Fig.3 were determined with the cooling rate  $q=0.5$  K/min in the ellipsometry experiment<sup>53</sup> by the relation  $\tau=T/q$  according to Schmelzer.<sup>61</sup> Thus, with the corroboration from the data of the two transitions observed by ellipsometry, we have strengthened the proposed identification of the segmental  $\alpha$ -relaxation and the sub-Rouse modes for the first and second processes in the two-step enthalpy recovery.

Presented in Fig.3 is the value of  $\tau_\alpha(T_g^l)=100$  s at  $T_g^l(h)$  for freestanding film with  $h=22$  nm deduced before from ellipsometry data<sup>40,41</sup>. Shown also are the few  $\tau_\alpha(T)$  data of the freestanding 22 nm PS film obtained from photon correlation spectroscopy<sup>60</sup>. The two black diamonds are the primitive relaxation time,  $\tau_0^{bulk}(T_g^{bulk})$ , of bulk PS at  $T_g^{bulk}=373$  K calculated by the CM equation<sup>20,24,25,26,27,29,-33</sup>,

$$\tau_{\alpha}(T) = [t_c^{-n(T)} \tau_0(T)]^{1/(1-n(T))} \quad (1)$$

by taking  $\tau_{\alpha}^{bulk}(T_g^{bulk}) = 10^2$  or  $10^3$  s,  $(1-n_{\alpha})$  equal 0.36 from PCS measurement of bulk PS<sup>62</sup>, and  $t_c=1$  to 2 ps the value of which was determined by neutron scattering<sup>20</sup>. The two are good estimates of the shortest  $\tau_{\alpha}$  that freestanding film may attain at the bulk  $T_g^{bulk}$  when the film becomes extremely thin, and  $n \rightarrow 0$ . The line in Fig.3 connects the PCS  $\tau_{\alpha}(T)$  of the 22 nm freestanding film<sup>60</sup>, the  $\tau_{\alpha}(T_g^l)=100$  s deduced from ellipsometry data for freestanding film thickness of 22 nm at  $T=T_g^l$ ,<sup>40,41</sup> and the primitive relaxation time of bulk PS  $\tau_0^{bulk}(T_g^{bulk})$  at  $T=T_g^{bulk}$ . The fact that the three data points lie approximately on a straight line is no accident because in the ultrathin 22 nm freestanding film cooperativity of the  $\alpha$ -relaxation is either totally or almost totally removed, and  $\tau_{\alpha}(T)$  becomes the same or almost the same as the primitive relaxation time  $\tau_0^{bulk}(T)$  of the bulk glass-former at *equilibrium* at temperatures below  $T_g^{bulk}$ , as discussed in more detail in ref.<sup>63</sup>. Thus the entire line in Fig.3 is a good approximation to the Arrhenius temperature dependence of the primitive relaxation time  $\tau_0^{bulk}(T)$  for all temperatures below  $T_g^{bulk}=373$  K.

Using eq.(1) once more and substituting this Arrhenius dependence of  $\tau_0^{bulk}(T)$  into its right-hand-side, the corresponding Arrhenius  $T$ -dependence of  $\tau_{\alpha}^{bulk}(T)$  is represented by the broken line in Fig.3. There is approximate order of magnitude agreement of the calculated  $\tau_{\alpha}^{bulk}(T)$  with  $\tau_{eq,1}$  of the first step in enthalpy recovery<sup>17,18</sup>. Conversely, by substituting  $\tau_{eq,1}(T)$  data (blue open circles) into the left-hand-side of eq.(1) we calculated the primitive relaxation times  $\tau_0^{bulk}(T)$  shown by green open triangles in Fig.3. There is also approximate agreement with the values of  $\tau_0^{bulk}(T)$  deduced by the other way (the two black diamonds). Consistency of the results substantiate that  $\tau_{eq,1}(T)$  has Arrhenius temperature dependence below  $T_g^{bulk}$  and not diverging<sup>58</sup>

in agreement with the conclusion of the same reached by McKenna and coworkers based on the study of million year old amber<sup>5,64</sup> and aging of other polymers<sup>5,65,66</sup>.

### 3. Discussion and Conclusion

The two-step enthalpy recovery deep in the glassy state of high and low molecular weight bulk polystyrene(PS) found by Cangialosi and coworkers is explained by attributing the first step to the segmental  $\alpha$ -relaxation and the second step to the sub-Rouse modes, and justified by the dynamic properties of the two processes elucidated by the Coupling Model (CM). The observation of twosteps in enthalpy recovery of bulk polystyrene by Cangialosi and co-workers has not been observed before in conventional heat capacity and volume recovery experiments. However, the two-step enthalpy recovery was found at much longer time scales of weeks or months and at temperatures further down below  $T_g$  than the conventional measurements. Thus it should be distinguished from the majority of experiments carried out at nominal cooling rates and temperature not far below  $T_g$ . The two-step enthalpy recovery also was found in nanometer freestanding PS thin films and nanospheres. The results from the PS thin films show on decreasing film thickness that the first step shifted to lower temperatures much more than the second step. These effects observed on the faster and slower processes in the two-step enthalpy relaxation bear strong resemblance to the behavior of the segmental  $\alpha$ -relaxation and the sub-Rouse modes in PS thin films, and hence support our explanation. Additional support comes from the fact that the segmental  $\alpha$ -relaxation and the sub-Rouse modes were used before to explain successfully two other effects observed on decreasing the thickness  $h$  of freestanding polystyrene films. One is the rubbery stiffening effect in creep compliance measurements caused by much large reduction of segmental  $\alpha$ -relaxation time  $\tau_\alpha(T)$  than the sub-Rouse relaxation time  $\tau_{sR}(T)$ . The other is the increasing separation between the lower and upper transition temperatures,  $T_g^l(h)$  and  $T_g^u(h)$ , on

decreasing  $h$  found by ellipsometry. Explained in the same way, these closely related effects help to confirm our explanation of the first and second steps of enthalpy recovery originating from the segmental  $\alpha$ -relaxation and the sub-Rouse modes respectively.

There are two very recent findings of a fast and a slow process in enthalpy relaxation. Although the two processes are not the segmental  $\alpha$ -relaxation and the sub-Rouse modes respectively in these cases, we mention them to contrast with the two-step enthalpy relaxation. One is from the differential scanning calorimetry study of several polymeric glasses aged over about 30 years well below their respective  $T_g$  when heated to the melt state<sup>67</sup>. The other is from fast scanning calorimetry study of the thermodynamic state attained after a given cooling rate and the molecular mobility of glassy poly(4-tert-butylstyrene) confined at the micrometer length scale<sup>68</sup>. The fast and slow processes observed in these two experiments are not the segmental  $\alpha$ -relaxation and the sub-Rouse modes of bulk polymers, and the explanation we give in this paper should not be applied. We believe the fast and slow processes in ref.<sup>67</sup> originate from the primitive relaxation/JG  $\beta$ -relaxation<sup>69</sup> and the segmental  $\alpha$ -relaxation respectively. This belief was made before in p.281 of ref.<sup>20</sup>, where cited are the enthalpy relaxation by DSC scan of the rapidly quenched glasses after annealing at temperature well below  $T_g$  apparently first applied by Chen and coworkers including polystyrene<sup>70</sup>, inorganic glasses ( $B_2O_3$ )<sup>71</sup>, and metallic glasses<sup>72,73,74,75</sup>. Chen and coworkers emphasized their observed relaxation at temperatures well below  $T_g$  by calling it sub-sub- $T_g$  relaxation. They also pointed out that the sub-sub- $T_g$  relaxations of polystyrene,  $B_2O_3$ , and metallic glasses are qualitatively similar in properties despite great differences in structure and bonding.

On the other hand, we believe the fast and slow processes in ref.<sup>68</sup> originate from the segmental  $\alpha$ -relaxation at and near the surface and the bulk part respectively of the micrometer



confined polymer. Incidentally, possible connection of this fast process to the volume-sensitive secondary relaxations<sup>68</sup> (this scenario is realized only when the length scales of confinement given by the volume-to-area ratio approach zero<sup>68</sup>) was made also by the authors of ref.<sup>68</sup>. The possible connection suggested<sup>68</sup> makes sense since volume-sensitive primitive/JG  $\beta$ -relaxations<sup>63</sup> is related to the segmental  $\alpha$ -relaxation at the surface<sup>32,58,63</sup>.

## REFEERENCES

- (1) Boucher, V. M.; Cangialosi, D.; Alegría, A.; Colmenero, J. Enthalpy Recovery of Glassy Polymers: Dramatic Deviations from the Extrapolated Liquidlike Behavior. *Macromolecules* **2011**, *44*, 8333–8342.
- (2) Cangialosi, D.; Boucher, V. M.; Alegría, A.; Colmenero, J. Direct Evidence of Two Equilibration Mechanisms in Glassy Polymers. *Phys. Rev. Lett.* **2013**, *111*, 095701
- (3) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A.R. Isobaric Volume and Enthalpy Recovery of Glasses. II. A Transparent Multiparameter Model. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1097–1162.
- (4) Hodge, I. M. Enthalpy Relaxation and Recovery in Amorphous Materials. *J. Non-Cryst. Solids* **1994**, *169*, 211–266.
- (5) McKenna, G. B.; Simon, S. L. 50th Anniversary Perspective: Challenges in the Dynamics and Kinetics of Glass-Forming Polymers. *Macromolecules* **2017**, *50*, 6333–6361.
- (6) Andreatti, L.; Faetti, M.; Giordano, M.; Palazzuoli, D.; Zulli, F. Enthalpy Relaxation in Polymers: A Comparison among Different Multiparameter Approaches Extending the TNM/AGV Model, *Macromolecules* **2003**, *36*, 7379-7387.
- (7) Hutchinson, J. M.; Kumar, P. Enthalpy Relaxation in Polyvinyl Acetate. *Thermochim. Acta* **2002**, *391* (1–2), 197–217.
- (8) Li, Q. X.; Simon, S. L. Enthalpy Recovery of Polymeric Glasses: Is the Theoretical Limiting Liquid Line Reached? *Polymer* **2006**, *47*, 4781–4788.
- (9) Simon, S. L.; Sobieski, J. W.; Plazek, D. J. Volume and Enthalpy Recovery of a Polystyrene. *Polymer* **2001**, *42* (6), 2555–2567.

- (10) Robertson, C. G.; Wilkes, G. L. Long-Term Volume Relaxation of Bisphenol A Polycarbonate and Atactic Polystyrene. *Macromolecules* **2000**, *33*, 3954–3955.
- (11) Koh, Y. P.; Simon, S. L. Enthalpy Recovery of Polystyrene: Does a Long-Term Aging Plateau Exist? *Macromolecules* **2013**, *46*, 5815–5821.
- (12) Cangialosi, D.; Boucher, V. M.; Alegria, A.; Colmenero, J., Physical aging in polymers and polymer nanocomposites: recent results and open questions. *Soft Matter* **2013**, *9*, 8619–8630.
- (13) Cangialosi, D. Dynamics and thermodynamics of polymer glasses. *J. Phys.: Condens. Matter* **2014**, *26*, 153101.
- (14) Cangialosi, D.; Alegria, A.; Colmenero, J. Effect of nanostructure on the thermal glass transition and physical aging in polymer materials. *Prog. Polym. Sci.* **2016**, *54–55*, 128–147.
- (15) Koh, Yung P.; Gao, Siyang; Simon, Sindee L. Structural recovery of a single polystyrene thin film using Flash DSC at low aging temperatures, *Polymer* **2016**, *96*, 182-187.
- (16) Koh, Yung P.; Simon, Sindee L. Enthalpy recovery of ultrathin polystyrene film using Flash DSC, *Polymer* **2018**, *143*, 40-45.
- (17) Boucher, Virginie M.; Cangialosi, Daniele; Alegría, Angel; Colmenero, Juan, Complex nonequilibrium dynamics of stacked polystyrene films deep in the glassy state, *J. Chem. Phys.* **2017**, *146*, 203312.
- (18) Boucher, Virginie M.; Cangialosi, Daniele; Alegría, Angel; Colmenero, Juan, Reaching the ideal glass transition by aging polymer films, *Phys.Chem.Chem.Phys.*, **2017**, *19*, 961-965.
- (19) Perez-De-Eulate Natalia G.; Cangialosi, Daniele Double Mechanism for Structural Recovery of Polystyrene Nanospheres, *ACS Macro Lett.* **2017**, *6*, 859–863.
- (20) Ngai, K.L., *Relaxation and Diffusion in Complex Systems*, Springer (New York) **2011**.
- (21) Plazek, D.J.; Ngai, K.L., Identification of different modes of molecular motion in polymers that cause thermorheological complexity, *Rubb.Chem.Tech.*, **1995**, *68*, 376-434.
- (22) Plazek, D.J.; Chay, I-C, Ngai, K.L.; Roland, C.M. Viscoelastic properties of polymers.4. Thermorheological complexity of the softening dispersion in polyisobutylene, *Macromolecules* **1995**, *28*, 6432-6436.
- (23) Rizos, A.K.; Jian, T.; Ngai, K.L. Determination of the Coupling Parameter of Local Segmental Motion in Poly(isobutylene) by Photon Correlation Spectroscopy, *Macromolecules* **1995**, *28*, 517-521

- (24) Plazek, D. J.; Bero, C. A.; Neumeister, S.; Floudas, G.; Fytas, G.; Ngai, K. L. Viscoelastic properties of amorphous polymers 3: low molecular weight poly(methylphenylsiloxane), *Colloid Polym. Sci.* **1994**, *272*, 1430-1438.
- (25) Ngai, K.L.; Plazek, D.J.; Rizos, A.K. Viscoelastic properties of amorphous polymers. 5. A coupling model analysis of the thermorheological complexity of polyisobutylene in the glass-rubber softening dispersion, *J. Polym. Sci. Part B Polym. Phys.* **1997**, *35*, 599-614.
- (26) Ngai, K.L.; Plazek, D.J., Resolution of sub-rouse modes of polystyrene by dissolution, *Macromolecules* **2002**, *35*, 9136-9141.
- (27) Xuebang Wu, Changsong Liu, Zhengang Zhu, K. L. Ngai, and Li-Min Wang, Nature of the Sub-Rouse Modes in the Glass\_Rubber Transition Zone of Amorphous Polymers, *Macromolecules* **2011**, *44*, 3605–3610.
- (28) Wu, Xuebang; Liu C.S.; Ngai, K.L. Origin of the crossover in dynamics of the sub-Rouse modes at the same temperature as the structural  $\alpha$ -relaxation in polymers, *Soft Matter* **10**, **2014**, 9324-9330.
- (29) Xuebang Wu, Huaguang Wang, Zhengang Zhu, and C. S. Liu, Quantifying Changes in the Low-Frequency Dynamics of Amorphous Polymers by 2D Correlation Mechanical Spectroscopy, *J. Phys. Chem. B* **2013**, *117*, 467–472.
- (30) Paluch, M.; Pawlus, S.; Sokolov, A. P.; Ngai, K. L. Sub-Rouse Modes in Polymers Observed by Dielectric Spectroscopy *Macromolecules* **2010**, *43*, 3103.
- (31) K. L. Ngai, Daniele Prevosto, Luigi Grassia, Viscoelasticity of Nanobubble-Inflated Ultrathin Polymer Films: Justification by the Coupling Model, *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 214–224.
- (32) Ngai, K.L.; Prevosto, D.; Capaccioli, S. A perspective on experimental findings and theoretical explanations of novel dynamics at free surface and in freestanding thin films of polystyrene, *Philos. Mag.* **2016**, *96*, 854-869.
- (33) Ngai, and D. J. Plazek, Thermo-Rheological, Piezo-Rheological, and  $TV^\gamma$ -Rheological Complexities of Viscoelastic Mechanisms in Polymers, *Macromolecules* **2014**, *47*, 8056–8063. Floudas, G.; Reisinger, T. Pressure dependence of the local and global dynamics of polyisoprene, *J. Chem. Phys.* **1999**, *111*, 5201.
- (34) Floudas, G.; Reisinger, T. Pressure dependence of the local and global dynamics of polyisoprene, *J. Chem. Phys.* **1999**, *111*, 5201.
- (35) Floudas, G.; Gravalides, C.; Reisinger, T. G.; Wegner, Effect of pressure on the segmental and chain dynamics of polyisoprene. Molecular weight dependence, *J. Chem. Phys.* **1999**, *111*, 9847.

- (36) Floudas, G. Effects of pressure on systems with intrinsic orientational order, *Prog. Polym. Sci.* **2004**, *29*, 1143.
- (37) Kriegs, H.; Gapinski, J.; Meier, G.; Paluch, M.; Pawlus, S.; Patkowski, A. Pressure effects on the  $\alpha$  and  $\alpha'$  relaxations in polymethylphenylsiloxane, *J. Chem. Phys.* **124**, 104901 (2006).
- (38) Roland, C. M.; Paluch, M.; Casalini, R. Effects of the Volume and Temperature on the Global and Segmental Dynamics in Poly(propylene glycol) and 1,4-Polyisoprene *J. Polym. Sci. B: Polym. Phys.* **2004**, *42*, 4313.
- (39) Ngai, K.L.; Casalini, R.; Roland, C.M. Volume and Temperature Dependences of the Global and Segmental Dynamics in Polymers: Functional Forms and Implications for the Glass Transition, *Macromolecules* **2005**, *38*, 4363.
- (40) Ngai, K. L.; Capaccioli, S.; Prevosto, D. Sub-Rouse modes in polymer thin films: Coupling to density and responding to physical aging, *AIP Conference Proceedings* **2016**, *1736*, 020006.
- (41) Prevosto, D.; Capaccioli, S.; Ngai, K. L. Origins of the Two Simultaneous Mechanisms Causing Glass Transition Temperature Reductions in High Molecular Weight Freestanding Polymer Films. *J. Chem. Phys.* **2014**, *140*, 074903 (1–9).
- (42) Korus, J.; Beiner, M.; Busse, K.; Kahle, S.; Unger, R.; Donth, E. Heat capacity spectroscopy at the glass transition in polymers, *Thermochimica Acta* **1997**, *304/305*, 99-110.
- (43) Weyer, S.; Hensel, A.; Korus, J.; Donth, E.; Schick, C. Broad band heat capacity spectroscopy in the glass-transition region of polystyrene, *Thermochimica Acta* **1997**, *304/305*, 251-255.
- (44) Ngai, K.L.; Plazek, D.J.; Rendell, R.W. Some examples of possible descriptions of dynamic properties of polymers by means of coupling model, *Rheol. Acta* **1997**, *36*, 307-319.
- (45) O'Connell, P.A.; McKenna, G.B. Rheological measurements of the thermoviscoelastic response of ultrathin polymer films, *Science* **2005**, *307*, 1760-1763.
- (46) O'Connell, P.A.; Hutcheson, S.A.; McKenna, G.B. Creep behavior of ultra-thin polymer films, *J. Polym. Sci. Part B Polym. Phys.* **2008**, *46*, 1952-1965.
- (47) O'Connell, P. A.; Wang, J.; Ishola, T.; McKenna, G. B. Exceptional property changes in ultrathin films of polycarbonate: Glass Temperature, Rubbery Stiffening, and Flow. *Macromolecules* **2012**, *45* (5), 2453–2459.
- (48) Zhai, M.; McKenna, G.B. Elastic modulus and surface tension of a polyurethane rubber in nanometer thick films, *Polymer* **2014**, *55*, 2725-2733.
- (49) Li, X.; McKenna, G.B. Ultrathin polymer films: rubbery stiffening, fragility, and  $T_g$  reduction, *Macromolecules* **2015**, *48*, 6329-6336.

- (50) H. Yoon; McKenna, G. B. Dynamic and temperature dependent response of physical vapor deposited Se in freely standing nanometric thin films. *J. Chem. Phys.* **2016**, *144*, 184501.
- (51) Yoon, Heedong; McKenna, Gregory B. “Rubbery Stiffening” and Rupture Behavior of Freely Standing Nanometric Thin PIB Films, *Macromolecules* **2017**, *50*, 9821–9830.
- (52) Nguyen, Hung K.; Fujinami, So; Nakajima, Ken, Size-dependent elastic modulus of ultrathin polymer films in glassy and rubbery states, *Polymer* **2016**, *105*, 64-71.
- (53) Pye, J.E.; Roth, C. B. Two Simultaneous Mechanisms Causing Glass Transition Temperature Reductions in High Molecular Weight Freestanding Polymer Films as Measured by Transmission Ellipsometry, *Phys. Rev. Lett.* **2011**, *107*, 235701.
- (54) Dalnoki-Veress, K.; Forrest, J. A.; Murray, C.; Gigault, C.; Dutcher, J. R. Molecular weight dependence of reductions in the glass transition temperature of thin freely standing polymer films, *Phys. Rev. E* **2001**, *63*, 031801.
- (55) Rotella, C.; Napolitano, S.; Wubbenhorst, M. Segmental Mobility and Glass Transition Temperature of Freely Suspended Ultrathin Polymer Membranes, *Macromolecules* **2009**, *42*, 1415.
- (56) Napolitano, S.; Wubbenhorst, M. Structural relaxation and dynamic fragility of freely standing polymer films, *Polymer* **2010**, *51*, 5309-5312.
- (57) Alcoutlabi, M.; McKenna, G. B. Effects of confinement on material behaviour at the nanometre size scale, *J. Phys.: Condens. Matter* **2005**, *17*, R461–R524
- (58) Ngai, K. L. Interpreting the Dynamics of Nano-Confined Glass-Formers and Thin Polymer Films: Importance of Starting from a Viable Theory for the Bulk, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2980.
- (59) Pye, Justin E.; Roth, Connie B. Above, Below, and In-Between the Two Glass Transitions of Ultrathin Free-Standing Polystyrene Films: Thermal Expansion Coefficient and Physical Aging, *J. Polym. Sci., Part B: Polym. Phys.* **2015**, *53*, 64–75.
- (60) Forrest, J. A.; Svanberg, C.; Revesz, K.; Rodahl, M.; Torell, L. M. & B. Kasemo; Relaxation Dynamics in Ultrathin Polymer Films, *Phys. Rev. E* **1998**, *58*, R1226.
- (61) Schmelzer J., Kinetic criteria of glass formation and the pressure dependence of the glass transition temperature *J. Chem. Phys.* **2012**, *136*, 074512.
- (62) Lindsey, C.P.; Patterson G.D., Stevens, J.R., Photon Correlation Spectroscopy of Polystyrene near the Glass-Rubber Relaxation, **1979**, *J. Polym. Sci. Part B. Polym. Phys.* *17*, 1547.
- (63) Ngai, K. L.; Capaccioli, Simone; Paluch, Marian; Prevosto, Daniele, Temperature Dependence of the Structural Relaxation Time in Equilibrium below the Nominal  $T_g$ : Results from Freestanding Polymer Films, *J. Phys. Chem. B* **2014**, *118*, 5608–5614

- (64) Zhao, J.; Simon, S. L.; McKenna, G. B. Using 20-Million-Year-Old Amber to Test the Super-Arrhenius Behaviour of Glass-Forming Systems. *Nat. Commun.* **2013**, *14*, 1783.
- (65) O'Connell, P. A.; McKenna, G. B. Arrhenius-Type Temperature Dependence of the Segmental Relaxation Below  $T_g$ . *J. Chem. Phys.* **1999**, *110*, 11054.
- (66) McKenna, G. B.; Zhao, J. Accumulating Evidence for Non-Diverging Time-Scales in Glass-Forming Fluids. *J. Non-Cryst. Solids* **2015**, *407*, 3–13.
- (67) Perez-De Eulatea, Natalia G.; Cangialosi, Daniele, The very long-term physical aging of glassy polymers *Phys.Chem.Chem.Phys.* **2018**, *20*, 12356.
- (68) Monnier, Xavier; Cangialosi, Daniele, Thermodynamic Ultrastability of a Polymer Glass Confined at the Micrometer Length Scale *Phys. Rev. Lett.* **2018**, *121*, 137801.
- (69) Ngai, K.L.; Paluch, M. Classification of secondary relaxation in glass-formers based on dynamic properties, *J. Chem. Phys.* **2004**, *120*, 857-873.
- (70) Chen, H.S.; Wang, T.T. Sub-sub  $T_g$  structural relaxation in glassy polymers, *J. Appl. Phys.* **1981**, *52*, 5898.
- (71) Chen, H.S.; Kurkjian, C.R. Sub-sub- $T_g$  enthalpy relaxation in a  $B_2O_3$  glass, *J. Am. Ceram. Soc.* **1983**, *66*, 613-619.
- (72) Chen, H.S. On Mechanisms of structural relaxation in a  $Pd_{48}Ni_{32}P_{20}$  glass, *J. Non-Cryst. Solids* **1981**, *46*, 289-305.
- (73) Inoue, A.; Masumoto, T.; Chen, H.S. Two-stage enthalpy relaxation behavior of  $(Fe_{0.5}Ni_{0.5})_{83}P_{17}$  and  $(Fe_{0.5}Ni_{0.5})_{83}B_{17}$ , *J. Mater. Sci.* **1985**, *20*, 2417-2438.
- (74) Hu, Lina; Zhang, Chunzhi; Yue, Yuanzheng, Structural evolution during the sub- $T_g$  relaxation of hyperquenched metallic glasses, *Appl.Phys.Lett.* **2010**, *96*, 221908-3.
- (75) Aji, D. P. B.; Johari, G. P., Kinetic-freezing and unfreezing of local-region fluctuations in a glass structure observed by heat capacity hysteresis, *J. Chem. Phys.* **2015**, *142*, 214501-9.
- (76) Song, Lijian; Xu, Wei; Huo, Juntao; Wang, Jun-Qiang; Wang, Xinmin; Li, Runwei, Two-step relaxations in metallic glasses during isothermal annealing, *Intermetallics* **2018**, *93*, 101–105.