



# The very long-term physical aging of glassy polymers

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The thermodynamic behavior of glasses well below the glass transition temperature ( $T_g$ ) is scarcely explored due to the long time scales required for such investigation. Here, we characterize the thermodynamic state of several polymer glasses aged for about 30 years at room temperature, that is, at more than 100 K below their respective  $T_g$ (s). To this aim we employ differential scanning calorimetry (DSC), which, *via* specific heat, allows characterizing the enthalpy attained after a certain aging protocol and the way the glass with such an enthalpy devitrifies when heated. We complement these results with extensive DSC studies on these polymers aged under the same conditions of temperature for time scales ranging from minutes to months. The main outcome of the present work is that these polymers aged under these conditions reach a plateau in the enthalpy with partial enthalpy recovery and devitrify well below  $T_g$ . This result provides compelling evidence for the existence of a fast mechanism of equilibrium recovery, beyond the standard slow one in proximity of  $T_g$ . The analogy with other kinds of glasses is highlighted, stigmatizing the universality of such behavior. Finally, the way the fast mechanism of equilibrium recovery could be exploited to obtain glasses with a low energy state is discussed.

## 1 Introduction

Physical aging or structural recovery is a well-known phenomenon entailing the densification of a glass previously cooled below its glass transition temperature,  $T_g$ .<sup>1–6</sup> It originates from the non-equilibrium nature of glasses, whose free energy decreases with time toward the metastable thermodynamic equilibrium represented by the supercooled liquid. The reason why a non-equilibrium glass is obtained resides in the inability of the supercooled liquid to rearrange in the time scale of the

experiment, defined by the inverse of the cooling rate employed to obtain the glass. Such a time scale defines the  $T_g$ , which, as a consequence, exhibits pronounced cooling rate dependence.<sup>7</sup>

Given these premises, the classic description of physical aging is based on the monotonous evolution of the thermodynamic state toward equilibrium,<sup>1</sup> on a time scale intimately connected to the so-called  $\alpha$  relaxation, with strong temperature dependence often described by the Vogel–Fulcher–Tammann (VFT) equation.<sup>8–10</sup> Hence, within such a description, only one molecular mechanism and its associated time scale are considered in different approaches.<sup>11–18</sup> These are generally adequate to describe physical aging in proximity of  $T_g$ , although it must be pointed out that some old studies put forward the possibility that a more complex behavior of physical aging, based on sequential relaxations, exists.<sup>19,20</sup> More recently, the paradigm based on a single molecular mechanism has been challenged by carrying out physical aging experiments over long time scales and significantly below  $T_g$ . In particular, several studies provided evidence for the existence of multiple mechanisms of equilibrium recovery in different glasses, including polymers,<sup>21–27</sup> low molecular weight glass formers,<sup>28,29</sup> chalcogenides,<sup>30,31</sup> and metallic glasses.<sup>32,33</sup> In these studies, either the way recovery of equilibrium,<sup>21,24,26,29</sup> devitrification on heating,<sup>25,27,28</sup> or vitrification on cooling<sup>23,34</sup> take place, was found to proceed in two or more steps. The slowest of such steps was found to depend on the aging temperature in ways analogous to the  $\alpha$  relaxation with VFT behavior.<sup>24,26,33</sup> In contrast, the temperature dependence of the fast mechanism of equilibrium recovery, when scrutinized conducting aging experiments over a wide temperature range, was found to exhibit low activation energy, amenable to a description by the Arrhenius law.<sup>24,26,33</sup>

In the context of the mentioned recent studies, it has to be pointed out that, while the observation of different steps of equilibrium recovery requires relatively short time scales in confined glasses,<sup>25,26</sup> the same observation requires aging time scales always larger than several weeks,<sup>24,27,33</sup> or even years<sup>21,22,30,31</sup> in bulk glasses. As a result the way bulk glasses

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aged over very long time scales, and its analogy with confined glasses,<sup>35,36</sup> well below  $T_g$  remains vastly unexplored.

In the present work, we employ differential scanning calorimetry (DSC) to unveil how several polymeric glasses aged over about 30 years well below their respective  $T_g$  devitrify when heated to the melt state. Furthermore, we complement these data with additional DSC experiments on the same polymers aged for times ranging from minutes to several months under conditions of temperature essentially equal to those of samples aged for 30 years. Our results indicate that devitrification of these samples proceeds *via* two distinct mechanisms. Apart from the slow one, responsible for the devitrification in proximity of the polymers'  $T_g$ , a fast mechanism is detected. The fact that the aging is conducted far below  $T_g$  implies that, differently from glasses aged in proximity of  $T_g$ ,<sup>24</sup> devitrification takes place in a temperature range considerably below that associated with the glass transition temperature; and recovery of equilibrium proceeds to a plateau with the thermodynamic state exhibiting enthalpy much larger than that of the extrapolated supercooled liquid.

## 2 Experimental section

The following amorphous polymers were employed in the present study: (1) poly(arylate) (PAr), purchased from Union Carbide with  $M_n = 22\,700\text{ g mol}^{-1}$  and  $M_w/M_n = 1.27$ ; (2) poly(bisphenol-A-carbonate) (PC), purchased from Bayer with  $M_n = 23\,600\text{ g mol}^{-1}$  and  $M_w/M_n = 1.22$ ; and (3) polysulfone (PSU), purchased from Union Carbide with  $M_n = 57\,000\text{ g mol}^{-1}$  and  $M_w/M_n = 1.28$ . In all cases the molecular weight was characterized by size exclusion chromatography (SEC). The  $T_g$  values obtained by DSC upon cooling at  $20\text{ K min}^{-1}$  considering the mid-point of the step in the specific heat are summarized in Table 1 together with the specific heat step at  $T_g$ . Prior to their use, all polymers were stored in a dry atmosphere during about 30 years ( $\sim 10^9\text{ s}$ ).

Calorimetric measurements were performed using a DSC-Q2000 calorimeter from TA-Instruments, calibrated with melting indium. The temperature control consisted of a DSC refrigerated cooling system by TA instruments. The nitrogen line is based on a highly dried gas, obtained from the direct evaporation of liquid nitrogen. A nitrogen flow was warranted during the thermal cycles used to obtain specific heat scans. Since the calorimeter directly delivers the heat flow rates, from the sample mass the specific heat was readily obtained. Samples aged for about 30 years were first placed in DSC pans with a weight ranging from 1 to 5 mg, cooled to 183 K and heated at  $10\text{ K min}^{-1}$  while recording specific heat data at a temperature considerably above the polymer  $T_g$ . This was 523 K for PSU and PAr and

473 K for PC. In such a way the samples' thermodynamic state after  $\sim 30$  years aging was assessed and the previous thermal history erased. All samples were subsequently cooled at  $20\text{ K min}^{-1}$  to 183 K and immediately heated to room temperature (296 K) for aging times between 2 min and 60 days. After annealing, the samples were again cooled to 183 K and heated to above  $T_g$  at  $10\text{ K min}^{-1}$  for specific heat data collection. For aging times shorter than one week, annealing was carried out inside the DSC, whereas vacuum ovens were employed for larger times. The temperature in the oven was monitored continuously using a thermometer placed beside the samples. Oscillations from the setpoint value of 296 K of  $\pm 1\text{ K}$  were detected. For the sake of reproducibility, at least three samples were employed for each aging time. The thermodynamic state attained after aging at room temperature was specified in terms of the fictive temperature ( $T_f$ ), that is, the temperature at which the glass line – drawn from the state of a glass obtained after a given thermal history – intersects the extrapolated melt line.<sup>37</sup> This implies that low  $T_f$ (s) corresponds to low energy glasses and, glasses aged for an infinite time at a given aging temperature  $T_a$ , would attain the thermodynamic state of the extrapolated melt line with  $T_f = T_a$ .  $T_f$  was obtained using the Moynihan method:<sup>12</sup>

$$\int_{T_f}^{T \gg T_g} (C_{pm} - C_{pg}) dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg}) dT \quad (1)$$

where  $C_{pm}$  and  $C_{pg}$  are the specific heat of the melt and the glass, respectively.

## 3 Results & discussion

The calorimetric signature of devitrification of a glass with a given thermodynamic state generally consists of two components:<sup>38</sup> (i) the variation from the specific heat of the glass to that of the melt, that is, the reversing part of the specific heat; (ii) the contribution resulting from the irreversibility, in the thermodynamic sense, of the glass transition. The latter component results in the presence of an overshoot whose magnitude depends on the thermodynamic state of the glass. For glasses aged over relatively short times close to  $T_g$ , such overshoot is generally located in proximity of the step in the specific heat underlying the devitrification of the glass.

Given these premises, we start presenting specific heat scans at  $10\text{ K min}^{-1}$  for all investigated polymers aged at room temperature at the indicated aging times. These are shown in panels a–c of Fig. 1. A first inspection of this figure indicates that the step in the specific heat in proximity of the polymer  $T_g$  is essentially unaffected by aging. Rather the signature of the change in the thermodynamic state of the glass during physical aging is the development of a very broad overshoot in a temperature range of more than 100 K and whose onset is located far below  $T_g$ . A magnification of data shown in Fig. 1a–c is presented in panels d–f of the same figure, where the specific heat of the aged sample in excess to that of the unaged reference is presented. As can be seen, the endothermic

**Table 1**  $T_g$  and specific heat step at  $T_g$  for all investigated polymers

Polymer	$T_g$ (K)	$\Delta c_p(T_g)$ ( $\text{J g}^{-1}\text{ K}^{-1}$ )
PAr	463	0.225
PC	423	0.23
PSU	459	0.225

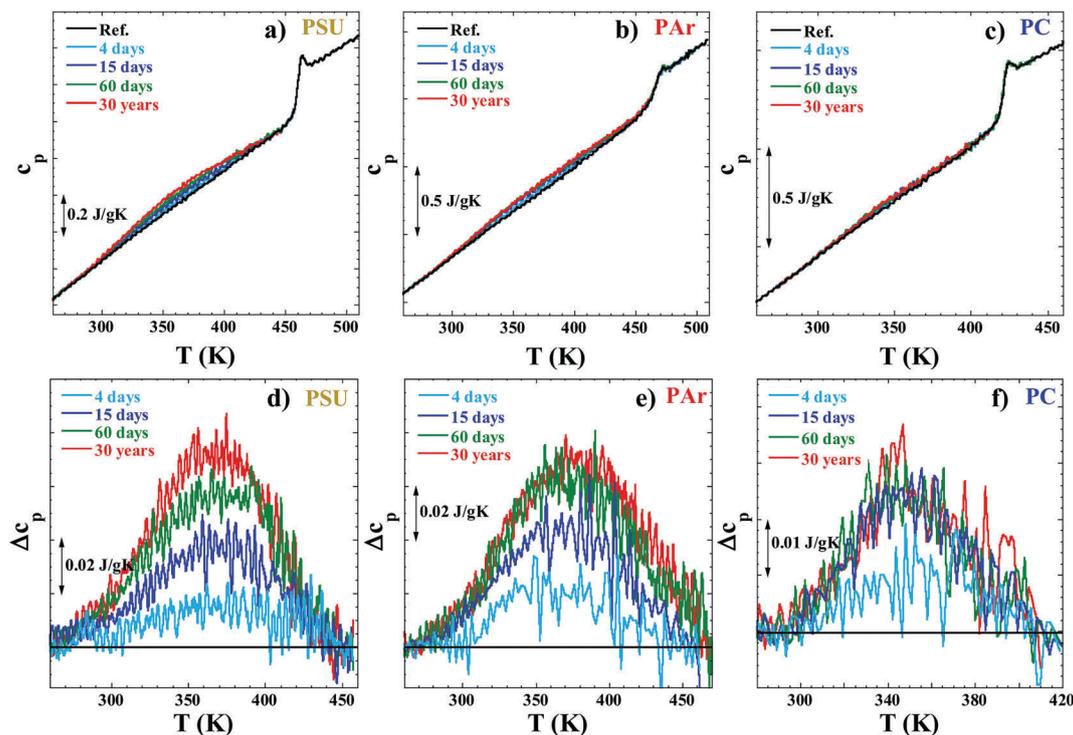


Fig. 1 Specific heat scans for samples aged at the indicated times at room temperature and the unaged references (panels a–c); and the corresponding specific heats in excess to the unaged reference in the temperature range where the endothermic overshoot underlying enthalpy recovery is visible (panels d–f).

overshoot, though tiny, is visible after four days of aging and becomes prominent with longer aging times. An analogous result was previously shown for polystyrene (PS) thin films,<sup>25,26</sup> and for a plastic crystal aged for seven years.<sup>28</sup> The endothermic overshoot observed well below  $T_g$  may also bear some relation with the so-called “pre-peak” or “second glass transition”, well documented in different glasses – including polymers,<sup>39,40</sup> glassy water<sup>41</sup> and metallic glasses<sup>32,42</sup> – obtained after a variety of thermo-mechanical histories.

Data shown in Fig. 1 were analyzed to evaluate the aging time evolution of  $T_f$ , employing eqn (1). This is shown in Fig. 2 for all investigated polymer glasses. As a general observation, all polymers aged at room temperature exhibit a monotonous

decrease to a plateau after a time scale between  $10^6$  and  $10^7$  s. This means that the thermodynamic state of these glasses, after evolving in the first few months once produced upon cooling from the melt, remains essentially unaltered up to a time scale of about 30 years. However, it is important to notice that in all cases the  $T_f$  achieved at the plateau vastly deviates from the aging temperature  $T_a = 296$  K. In particular, values of  $T_f$  more than 100 K larger than  $T_a$  are found at such a plateau. This implies that only a portion of the total recoverable enthalpy, that is, that corresponding to the extrapolated liquid line, is actually recovered at the plateau. This result is in line with a wide range of reports also showing partial recovery of equilibrium after aging significantly below  $T_g$ .<sup>43–51</sup>

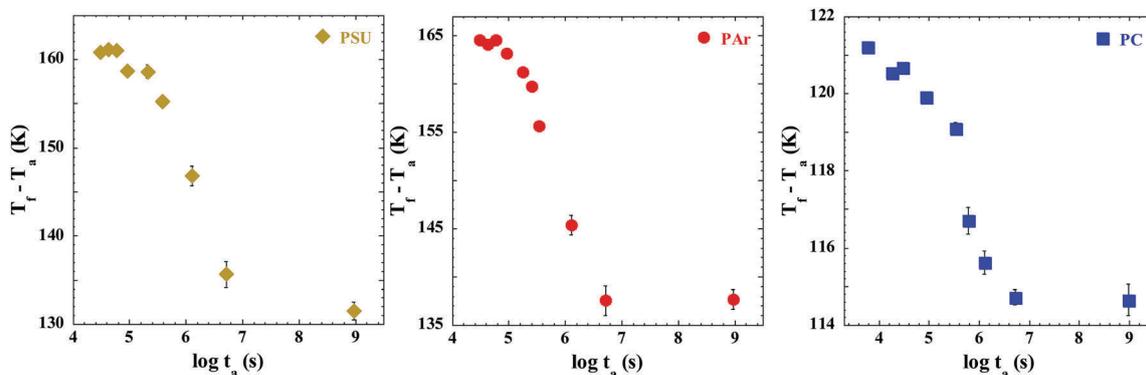


Fig. 2 Aging time dependence of the fictive temperature for all investigated polymers aged at room temperature.

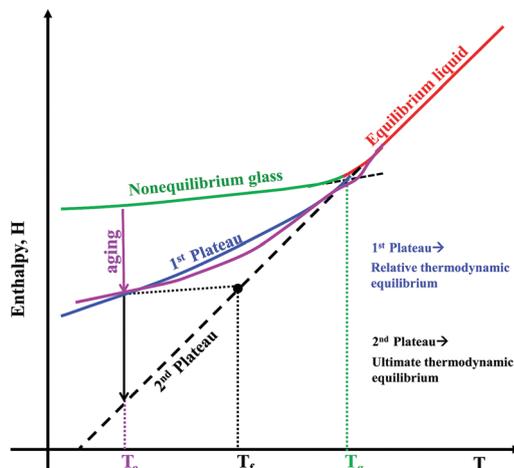


Fig. 3 Schematic thermodynamic plot showing the thermodynamic equilibria accessible upon aging a glass obtained upon cooling from the equilibrium melt. The way enthalpy is recovered upon heating from a state corresponding to the relative thermodynamic equilibrium with partial recovery is also shown (pink line).

Our results can be discussed within the framework of the presence of (at least) two mechanisms of equilibrium recovery, each drawing the glass to a metastable equilibrium. A scheme of the two mechanism/two metastable equilibrium state scenario is provided in Fig. 3. This figure qualitatively mimics the temperature dependence of the enthalpy of the investigated polymer glasses on the basis of the experimentally found behavior of the specific heat (see Fig. 1). With respect to the classic view of the thermodynamics of glasses,<sup>6</sup> the schematic plot of Fig. 3 shows the existence of an intermediate equilibrium, corresponding to partial equilibrium recovery, in line with the presence of a plateau with  $T_f \gg T_a$ , shown in Fig. 2. A similar picture was evidenced by extensive physical aging experiments in a temperature range somewhat closer to  $T_g$  in several glassy polymers.<sup>24</sup> Furthermore, the latter experiments showed further evolution toward complete equilibrium recovery. This provides indication that, if in the case of the present study time scales longer than 30 years were employed, a further decrease of the enthalpy would be observed *via* a slow mechanism of equilibrium recovery.

The aging time variation of the  $T_f$  shown in Fig. 2 indicates that the first plateau with partial recovery of equilibrium is reached after about  $10^7$  s. This implies that samples in this thermodynamic state, once heated up above the aging temperature, exhibit enthalpies larger than that of the final equilibrium but smaller than the partial equilibrium corresponding to the intermediate plateau. Given the fact that the time scale involved in the equilibrium recovery corresponding to the latter plateau is much shorter than that of the final plateau, heating above the aging temperature will result in an increase of the enthalpy. In other words, the initial step of devitrification takes place with an increase of the enthalpy toward the intermediate plateau. This is consistent with the observation of early devitrification, at temperatures much lower than  $T_g$ , observed in Fig. 2. Furthermore, the enormous broadening of the low

temperature overshoot can be understood if a low activation energy of the fast mechanism of equilibrium recovery is considered. In such a case a distribution of equilibration times naturally results in a broad devitrification range in the temperature domain.<sup>52</sup> Low values of the activation energy were actually found for the fast mechanism of equilibrium recovery in PS both in bulk<sup>24</sup> and in thin film geometry.<sup>26</sup>

An intriguing implication of our results is that the presence of a fast mechanism of equilibrium recovery results in a  $T_f$  decrease, which can be as large as 30 K. This is the case of PSU and PAR, while the  $T_f$  of PC only exhibits a drop of less than 10 K. In all cases, the decrease in  $T_f$  is significant and, importantly, is observed far below  $T_g$ , that is, at temperatures where the slow mechanism of equilibration is expected to reach geological time scales or even diverge according to the standard VFT behavior. Hence, our results indicate that, in contrast to the conventional view of physical aging, a massive decrease of the enthalpy toward equilibrium can be observed even in conditions under which the  $\alpha$  relaxation is expected to be essentially frozen. This highlights the utmost importance of heterogeneous dynamics, involving different molecular mechanisms, in the theoretical description of physical aging.<sup>53</sup>

Finally, it is worth pointing out that to observe experimentally detectable physical aging effects in bulk polymers in terms of excess specific heat (see Fig. 1) and  $T_f$  decrease (see Fig. 2) at least several days are required. Similarly, thick PS films showed an excess coefficient of thermal expansion by ellipsometry after aging for several months.<sup>27</sup> The same applies to a plastic crystal aged for several years, also exhibiting excess specific heat in ways analogous to the present study. However, recently it has been shown that confined polymers exhibiting a large amount of free interface<sup>54–56</sup> essentially exhibit the same phenomenology but on considerably shorter time scales.<sup>25,26</sup> This allowed accessing energy states with  $T_f$  corresponding to glasses with vanishing excess entropy;<sup>25</sup> a fact that was interpreted as a signature of the existence of the so-called “ideal” glass transition, long ago theorized by Gibbs and DiMarzio.<sup>57</sup>

## 4 Conclusions

The present work takes inspiration from recent findings showing the existence of multiple mechanisms of equilibrium recovery in different kinds of glasses. To achieve further insights into this issue, in the present work we have investigated the thermodynamic state of polymer glasses aged over about 30 years by DSC. This result is complemented with a wide range of additional results on the same polymers aged from minutes to several months. Our results indicate that these systems under these conditions age *via* a fast mechanism of equilibrium recovery. The signature of such mechanism consists of essentially two components: (1) the devitrification takes place at temperatures far below  $T_g$ , in a range where the typical mechanism associated with the  $\alpha$  relaxation is expected to exhibit geological relaxation times; (2) the plateaus in the enthalpy exhibit  $T_f$ (s) vastly different from the aging temperature, indicating that such

plateaus correspond to a relative equilibrium. These results show how glasses with low energy can be accessed by exploiting the fast mechanism of equilibrium recovery. We point out that, while the time scales involved even for such a mechanism are larger than weeks, employing confined glasses with a large amount of effectively free interface can provide a route to access low energy states in time scales accessible to the experimental practice.

## Conflicts of interest

There are no conflicts to declare.

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