

## Isothermal physical aging of thin PMMA films near the glass transition temperature

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Received: 25 December 2009 / Revised: 30 March 2010 / Accepted: 22 June 2010 /  
Published online: 6 July 2010  
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**Abstract** Isothermal physical aging and the glass transition temperature ( $T_g$ ) of PMMA thin films were investigated by means of differential scanning calorimetry (DSC). Freestanding thin films of different molecular weights ( $M_w = 120,000, 350,000, 996,000$  g/mol) and film thicknesses (40–667 nm) were obtained by spin coating onto a silicon wafer substrate and then releasing the coated film using a water floating technique. The thin films were stacked in a DSC pan and isothermally aged for different aging times ( $t_a = 1$  and 12 h) and aging temperatures ( $T_a = 105, 110, \text{ and } 115$  °C) below but near  $T_g$ . Enthalpy relaxation ( $\Delta H_{\text{Relax}}$ ), resulting from the isothermal physical aging, initially increased with increasing  $\Delta T$  ( $T_g - T_a$ , driving force of aging), reached a maximum value, and then decreased with further increase in  $\Delta T$ . Below  $\sim 100$  nm film thickness,  $\Delta H_{\text{Relax}}$  of samples aged near their  $T_g$  (i.e.,  $T_a = 110$  and  $115$  °C) decreased with decreasing film thickness, indicating the suppression of physical aging. Up to 9.9 °C depression in  $T_g$  was observed for thinner films ( $\sim 40$  nm), when compared to the thicker films ( $\sim 660$  nm) in this study. The decrease in  $\Delta H_{\text{Relax}}$  with decreasing film thickness at a given  $T_a$  appears to be associated with the reduction in  $T_g$ .

**Keywords** Physical aging · Thin film · PMMA · The glass transition temperature

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## Introduction

Physical aging always occurs in amorphous glassy polymers, which involves a gradual approach toward thermal equilibrium by a loss of thermodynamic excesses such as volume, enthalpy, and entropy. The technological significance of this phenomenon stems from the fact that the engineering properties (e.g., mechanical, dielectric, diffusivity) of the glasses depending on their thermodynamic properties are altered during physical aging [1].

Rapid progress in the usage and development of thinner polymer films for a variety of applications (such as coatings, lubrication, electronic packaging, and nanolithography processes) necessitates a better understanding of the properties of polymeric materials confined to the nano-scale. Although nanoconfinement effects have been widely investigated for polymers in the form of thin glassy films, physical aging behavior for the thin films are still a matter of contention. Both acceleration [2–5] and retardation [6, 7] of structural relaxation during physical aging for different types of nanoconfinement and materials have been reported. For example, physical aging was shown to accelerate for small molecules confined in nanopores due to smaller relaxation times at aging temperatures a given distance below the glass transition temperature [2]. Also, a shorter time to reach thermal equilibrium was observed in stacked thin polystyrene (PS) film [3]. The aging rate of submicron thin films of polysulfone and poly(2,6-dimethyl-1,4-phenylene oxide) was shown to increase with decreasing film thickness [4, 5]. In contrast, depressed aging was observed in PS thin films when compared to the bulk [6]. Retardation was also observed for polymethylmethacrylate (PMMA) thin films relative to the bulk due to the attractive interactions between the ester groups of PMMA and the hydroxyl groups of the silica substrate, restricting the segmental motion required for physical aging [7].

In addition to the physical aging of polymer materials, the nanoconfinement effects on the glass transition temperature ( $T_g$ ) have been extensively examined.  $T_g$  of polymer thin films is known to be reduced relative to the bulk unless strong interactions with a substrate are present [8–16]. For example, in freestanding PS thin films,  $T_g$  was depressed by about 70 °C over sample thickness variations of several tens of nanometers measured by Brillouin light scattering [9]. A 20 °C depression in  $T_g$  below 100 nm thickness of free standing PMMA thin film was observed via Ellipsometry [10]. Also, measurement of  $T_g$  by DSC was done for stacked PS specimens of 60 nm thickness free standing films, showing a smaller reduction of about 10 °C [8]. The smaller reduction for the stacked films relative to the freestanding film is attributed to inter-surface attraction between thin films, leading to restriction of segmental mobility in the free surfaces and therefore increased  $T_g$ . Even a highly crosslinked thermosetting thin film showed a  $T_g$  reduction of 15 °C for a film thickness of 40 nm, evaluated using modulated DSC [11].

In this study, we used a conventional differential scanning calorimetric (DSC) method to investigate the effect of film thickness on the isothermal physical aging and the glass transition temperature ( $T_g$ ) of PMMA thin films. Enthalpy relaxation due to the physical aging is conveniently monitored by DSC.

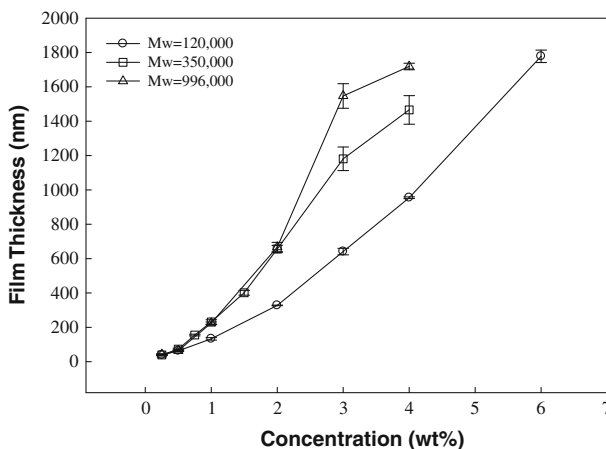
## Experimental

### Preparation of thin film

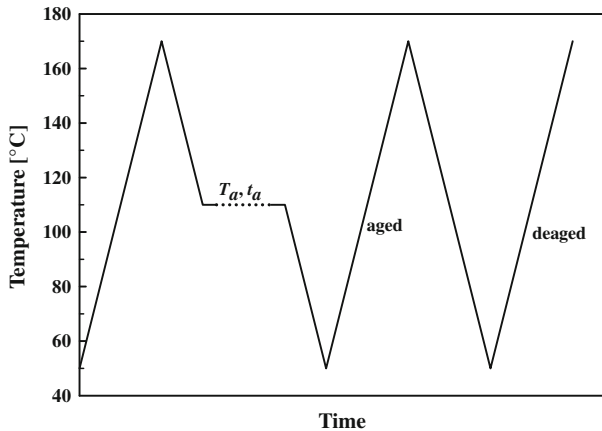
PMMA solutions of three different molecular weights ( $M_w = 120,000$ , 350,000 and 996,000 g/mol, Sigma-Aldrich Co., USA) were prepared by dissolving the polymer in chloroform (Sigma-Aldrich Co., USA) for 3 h at room temperature (23 °C) to yield solutions with polymer concentrations ranging from 0.25 to 6.0 wt%. A solution was deposited onto a 5-cm-diameter *n*-type silicon wafer (Semi-material Co., Korea) by means of a spin coater (Midas, spin1200 D, Korea). The initially stationary wafer was flooded with polymer solution until the entire surface was covered and then accelerated to a desired rotational rate (1000 rpm) for a spinning time of 60 s. The coated film was treated under vacuum at 140 °C for 1 h to remove the residual solvent. Film thickness measurements were performed using an Alpha-Step surface profiler (IQ, KLA-Tencor, USA). Figure 1 displays the film thickness as a function of concentration for the three different molecular weight PMMA samples. Based on the thickness data in Fig. 1, we selected concentrations of 1 and 3 wt% to yield film thickness of ~120 and ~650 nm, respectively, for  $M_w = 120,000$ . For  $M_w = 350,000$  and 996,000, 0.5 and 2 wt% concentrations were used to obtain ~40 and ~650 nm thickness, respectively. The deposited film was detached from the silicon wafer by dipping into distilled water and floating onto the water. Further details regarding the film preparation technique can be found in our previous report [17].

### DSC measurements

The floated film on the water was collected with a tweezer, and cut into small sizes before stacking into a DSC pan to obtain about 3 mg weight. Before clamping the



**Fig. 1** Film thickness as a function of polymer solution concentration for different PMMA molecular weights



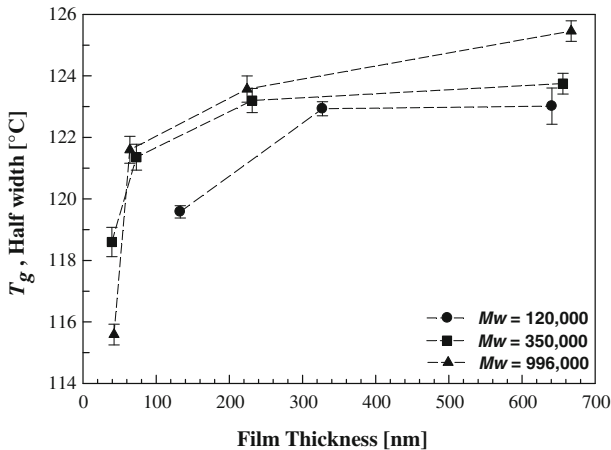
**Fig. 2** Time–temperature sequence

DSC pan with a cap, the stacked film sample was heated under vacuum at 70 °C for 1 h to remove trace amounts of water. The effect of physical aging for the stacked thin film was investigated by differential scanning calorimetry (Pyris 1 DSC, Perkin-Elmer, USA). The temperature–time sequence shown in Fig. 2 was then applied to the stacked films in the DSC pans. First, the specimen was heated to a temperature of 170 °C (40–50 °C above  $T_g$  of sample) to remove any pre-history of the sample, cooled to below  $T_g$ , and isothermally aged at an aging temperature ( $T_a$ ) for a pre-specified aging time ( $t_a$ ) to provide structural relaxation due to the isothermal physical aging. Immediately after the isothermal physical aging, two sequential up-temperature scans were made: the first up-scan included the isothermal aging effect (“aged”) and the second was used to determine the glass transition temperature (“de-aged”). Isothermal aging was performed at aging temperatures of 105, 110, 115 °C below but near the glass transition for aging times of 1 and 12 h. Heating and cooling rate in all experiments were fixed at 40 °C/min in a dry nitrogen gas atmosphere.

## Results and discussion

The glass transition temperature

The glass transition temperature of de-aged specimens was determined from the half-width of the step-wise transition on the DSC curves during the final heating scan in the temperature–time sequence (see Fig. 2). In Fig. 3, the  $T_g$  was plotted with respect to film thickness for all samples used in this study. In agreement with other work,  $T_g$  decreased with decreasing film thickness [8–16].  $T_g$  depression for  $M_w = 120,000$  and 350,000 was observed to be 3.4 °C ( $T_g = 123.0$  °C for thickness = 641 nm,  $T_g = 119.6$  °C for thickness = 133 nm) and 4.6 °C ( $T_g = 123.1$  °C for thickness = 656 nm,  $T_g = 118.5$  °C for thickness = 40 nm),



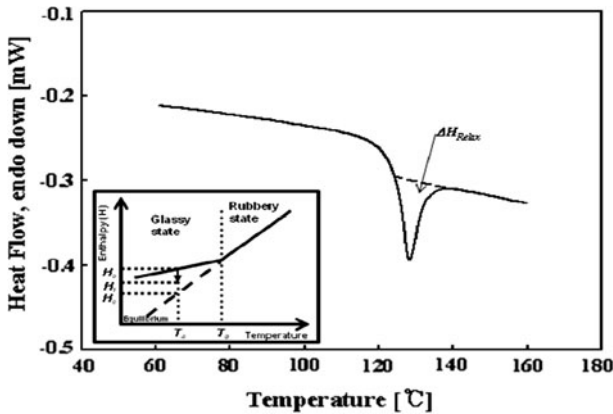
**Fig. 3** The glass transition temperature vs. film thickness for different molecular weights

respectively. For  $M_w = 996,000$ , a more prominent  $T_g$  depression by 9.9 °C ( $T_g = 125.5$  °C for thickness = 667 nm,  $T_g = 115.6$  °C for thickness = 42 nm) was observed. It should be noted that the  $T_g$  rapidly decreased below film thickness  $\sim 100$  nm for  $M_w = 350,000$  and 996,000. It was difficult to obtain film specimens below 100 nm thickness for  $M_w = 120,000$  because the coated film was too fragile to remove from a silicon wafer substrate. The  $T_g$  data present here are average values taken from at least three time–temperature sequences for each specimen.

### Physical aging

Structural relaxation due to isothermal physical aging near the glass transition in the glassy state gives rise to an endothermic peak in the vicinity of the glass transition region, an example of which is shown on the DSC curve in Fig. 4. The inset in this figure schematically shows the spontaneous reduction of enthalpy at a given aging temperature ( $T_a$ ) from  $H_o$  at  $t = 0$  to  $H_t$  at aging time ( $t$ ) ( $\Delta H_{\text{Relax}} = H_o - H_t$ ), until ultimately reaching  $H_e$  at equilibrium ( $\Delta H_{\text{Relax}} = H_o - H_e$ ). In this study, enthalpy relaxation values ( $\Delta H_{\text{Relax}}$ ) for samples isothermally aged at different aging temperatures ( $T_a = 105, 110, 115$  °C) and aging times ( $t_a = 1$  and 12 h) were determined from the area of the endothermic peak.

The physical aging process is generally considered to be a function of the deviation from the equilibrium state ( $\Delta T = T_g - T_a$ ) and the aging temperature ( $T_a$ ) [1]. The former is especially important when there are changes in  $T_g$  due to nanoconfinement. For example, PS thin film samples showed accelerated physical aging at a given aging temperature because of the reduction of  $T_g$  [10]. Therefore, it is necessary to examine the effect of physical aging at same  $\Delta T$  in order to observe film thickness effects on isothermal physical aging.  $\Delta H_{\text{Relax}}$  values, determined at the same  $\Delta T$  for each sample, were plotted versus  $\Delta T$  in Fig. 5 for  $M_w = 120,000$  (film thickness = 133, 327, 641 nm), 350,000 (film thickness = 40, 73, 231, 656 nm), and 996,000 (film thickness = 42, 64, 224, 667 nm). As shown in the



**Fig. 4** Determination of enthalpy relaxation value ( $\Delta H_{\text{Relax}}$ ) from a DSC heating scan (*Inset* shows schematic of physical aging process)

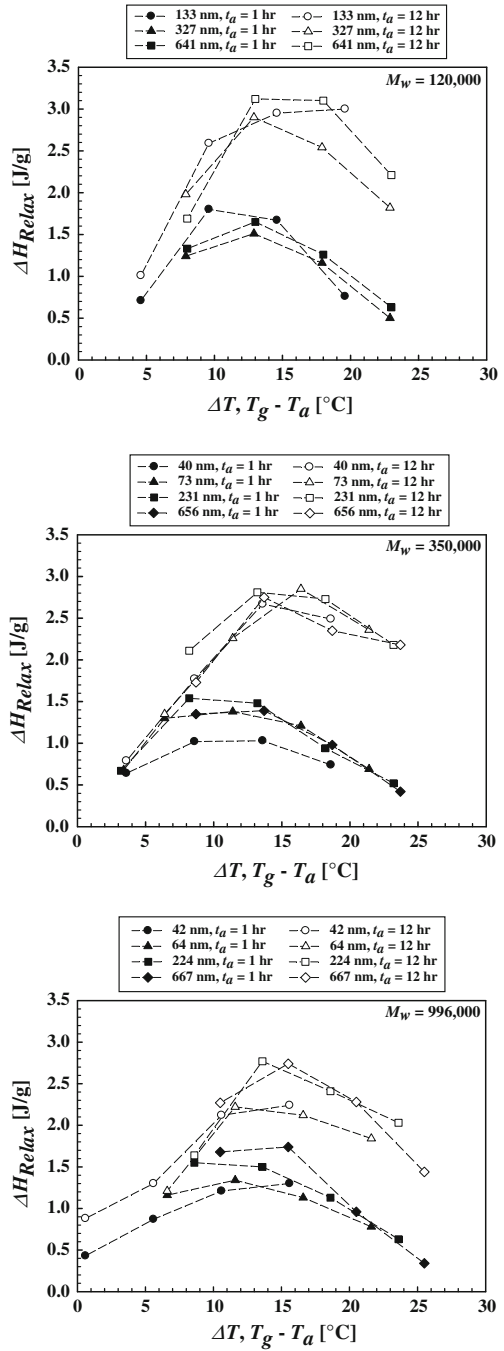
figure,  $\Delta H_{\text{Relax}}$  increased with increasing  $\Delta T$  (i.e., decreasing  $T_a$ ), reached a maximum, and then decreased as  $\Delta T$  increases further for all samples. Note that these maxima in  $\Delta H_{\text{Relax}}$  all occurred near  $\Delta T = 10\text{--}15\text{ }^\circ\text{C}$  ( $\Delta T_{\text{max}}$ ). Also, it is very clear from the figure that the longer aging time of 12 h gave larger  $\Delta H_{\text{Relax}}$ .

The  $\Delta H_{\text{Relax}}$  maximum is considered to arise from the combination of two temperature-dependent factors—the magnitude of  $\Delta H_\infty$  and segmental mobility. Once the aging sample reaches  $\Delta H_\infty$ , there will be no changes in enthalpy thereafter. The magnitude of  $\Delta H_\infty$  increases with increasing  $\Delta T$ , as seen in the inset of Fig. 4. The increase of  $\Delta H_{\text{Relax}}$  with increasing  $\Delta T$  below  $\Delta T_{\text{max}}$  is attributed to the changing  $\Delta H_\infty$  value of which the magnitude increases with increasing  $\Delta T$ . The decrease of  $\Delta H_{\text{Relax}}$  with increasing  $\Delta T$  above  $\Delta T_{\text{max}}$  is due to the restricted segmental motion at lower aging temperature, increasing the time required before equilibrium can be reached.  $\Delta H_{\text{Relax}}$  values at both  $t_a$  times of 1 and 12 h aging are nearly identical below  $\Delta T = 8\text{ }^\circ\text{C}$  for all three samples. This indicates that the samples reached equilibrium after 1 h of isothermal aging and no subsequent aging occurred thereafter.

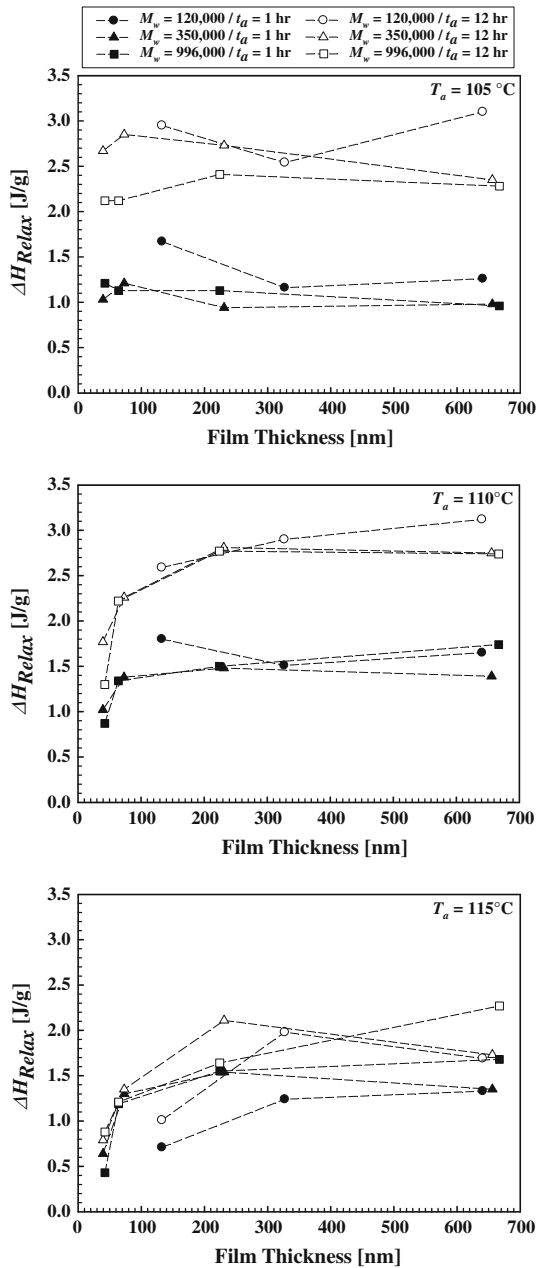
In order to examine the effect of film thickness on isothermal physical aging for  $M_w = 120,000$ , 350,000, and 996,000 g/mole,  $\Delta H_{\text{Relax}}$  versus film thickness is shown for  $T_a = 105$ , 110, and 115  $^\circ\text{C}$  in Fig. 6. At  $T_a = 105\text{ }^\circ\text{C}$ ,  $\Delta H_{\text{Relax}}$  was almost constant with respect to film thickness for both  $t_a = 1$  and 12 h. But, at  $T_a = 110\text{ }^\circ\text{C}$  and 115  $^\circ\text{C}$ ,  $\Delta H_{\text{Relax}}$  decreased below about 100 nm for 1 h of aging and below about 200 nm for 12 h of aging. The decrease in  $\Delta H_{\text{Relax}}$  for samples was most rapid below about 100 nm thickness at  $T_a = 110$  and 115  $^\circ\text{C}$ .

The free surface of amorphous polymers is reported to be liquid-like with less cohesive energy, enhanced mobility, and shorter relaxation time [6]. This provides an adequate explanation as to why, as measured in this study and reported in the literature [8–16], the  $T_g$  of thin films is lower than that of thick films. The gradient in the local segmental mobility across the film thickness (with the greatest mobility at the surface) leads to a localized glass transition temperature that increases when

**Fig. 5**  $\Delta H_{Relax}$  vs.  $\Delta T (= T_g - T_a)$  for samples with  $M_w = 120,000$ , 350,000, and 996,000



**Fig. 6**  $\Delta H_{\text{Relax}}$  vs. film thickness for samples with  $M_w = 120,000$ , 350,000, and 996,000



progressing from the free surface deeper into the film towards the bulk, until it coincides with the  $T_g$  of the bulk. Hence, the reduced  $T_g$  of the free surface results in a shift of the observed glass transition temperature towards lower temperatures by virtue of the fact that the free surface constitutes a greater fraction of the film for



thinner samples. Also, when the surface layer has a glass transition temperature close to  $T_a$  or lower than  $T_a$ , physical aging will be lessened or no longer occur, respectively, at the surface layer. Therefore, the total amount of physical aging becomes smaller in thinner films because the proportion of the surface layer is greater relative to total thickness. That the film thickness effect on the physical aging was not evident at the lower aging temperature of  $T_a = 105\text{ }^\circ\text{C}$  is presumably a result of the free surface  $T_g$  being near or slightly above  $105\text{ }^\circ\text{C}$  but likely below  $110\text{ }^\circ\text{C}$ . Note also that there was only a slight difference in  $\Delta H_{\text{Relax}}$  at  $t_a = 1$  and  $12\text{ h}$  at the highest aging temperature of  $T_a = 115\text{ }^\circ\text{C}$  (close to  $T_g$ ). As explained before, isothermal physical aging at  $T_a = 115\text{ }^\circ\text{C}$  reached almost the equilibrium state and no further aging takes place after  $1\text{ h}$  of aging.

In order to further understand effect of film thickness on the physical aging, the Kohlrausch–Williams–Watts (KWW) relaxation function,  $\phi(t)$ , was employed [18]. The kinetic process of approaching to thermal equilibrium can be expressed as a stretched exponential form;

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \quad (1)$$

where  $\beta$  (non-exponentiality parameter,  $0 < \beta \leq 1$ ) represents distribution of relaxation time, and  $\tau$  is the relaxation time. At a given aging temperature, the enthalpy relaxation process as a function of aging time is described by

$$\Delta H_{\text{Relax}}(t_a) = \Delta H_\infty[1 - \phi(t_a)] \quad (2)$$

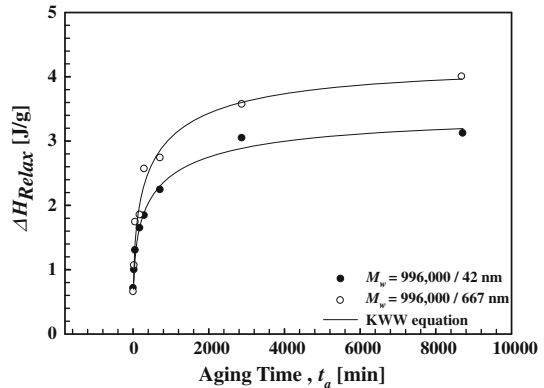
where  $\Delta H_\infty$  is the enthalpy at equilibrium. The adjustable parameters ( $\Delta H_\infty$ ,  $\beta$ , and  $\tau$ ) can be obtained from curve-fitting. This method has been reported elsewhere to study physical aging behavior of bulk PMMA [19, 20].

$\Delta H_{\text{Relax}}$  values were measured for film specimens ( $M_w = 996,000$ , film thicknesses =  $42$  and  $667\text{ nm}$ ) after isothermal aging at same  $\Delta T = 14.5 \pm 1\text{ }^\circ\text{C}$  for aging times of  $10, 30, 60, 180, 300, 720, 2880, 8690\text{ min}$ . The  $\Delta H_{\text{Relax}}$  versus aging time are displayed in Fig. 7 along with a curve-fitted solid line using Eq. 2. From the curve-fitting procedure,  $\beta$  was obtained to be  $0.38$  and  $0.41$ ,  $\Delta H_\infty$  to be  $3.37$  and  $4.13$ , and  $\tau$  to be  $500$  and  $476\text{ min}$  for  $42$  and  $667\text{ nm}$  film thicknesses, respectively. The lower value of  $\beta$  for the thinner film indicates the broader relaxation distribution which is consistent with other studies [21–24]. The larger relative portion of the surface layer in the thin films allows for the lower value of  $\Delta H_\infty$  and  $\tau$ . In order to accurately determine the fitting parameters, three aging experiments were performed to determine the average  $\Delta H_{\text{Relax}}$  for the last three aging times ( $720, 2880, \text{ and } 8690\text{ min}$ ).

## Conclusions

In this study, the effect of film thickness ranging from  $\sim 40$  to  $\sim 670\text{ nm}$  on isothermal physical aging was investigated for PMMA with different molecular weights by performing enthalpy measurements via differential scanning calorimetry. The glass transition temperature ( $T_g$ ) of stacked film was reduced by up to  $9.9\text{ }^\circ\text{C}$

**Fig. 7**  $\Delta H_{\text{Relax}}$  vs. aging time ( $t_a$ ) for different film thicknesses of 42 and 667 nm with  $M_w = 996,000$  (Solid line represents the curve-fitting of Kohlrausch–Williams–Watts function)



with decreasing film thicknesses, with a particularly rapid decrease occurring below 100 nm. Regardless of film thickness or aging time, enthalpy relaxation ( $\Delta H_{\text{Relax}}$ ) passes through a maximum value as  $\Delta T$  ( $= T_g - T_a$ ) increases. The  $\Delta H_{\text{Relax}}$  maximum may come from a combination of two effects—decreasing magnitude in  $\Delta H_{\infty}$  and increasing segmental mobility with increasing  $\Delta T$ . Below 100 nm film thickness at higher aging temperatures ( $T_a = 110$  and  $115$  °C), there was a rapid reduction in  $\Delta H_{\text{Relax}}$ . This reduction of  $\Delta H_{\text{Relax}}$  in the thinner film samples at a given aging temperature is presumably due to the  $T_g$  depression resulting from the larger fraction of free surface layer of the thin film. The film sample with 42 nm thickness exhibited broadening of the relaxation distribution and decreased magnitude of enthalpy at equilibrium, which was determined from the Kohlrausch–Williams–Watts (KWW) relaxation function.

**Acknowledgment** This research was supported by a Grant (03-K14-01-013-00) from Center for Nanoscale Mechatronics and Manufacturing, one of the 21st Century Frontier Research Programs, which are supported by Ministry of Science and Technology, Korea.

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