



# Study on enthalpy relaxation of polystyrene by assuming the existence of an intermediate aging plateau



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## ABSTRACT

The enthalpy relaxation of polystyrene (PS) is studied by assuming the existence of an intermediate aging plateau between the glass and the extrapolation of the liquid. The intermediate aging plateau is characterized by  $T_{gd}$  and  $\delta$  which represent the temperature below which the thermodynamic property deviates from the extrapolation of the liquid and the extent of the deviation. Both Tool–Narayanaswamy–Moynihan (TNM) and Adam–Gibbs–Vogel (AGV) equations are used to calculate the relaxation time.  $T_{gd}$  and  $\delta$  are obtained through fitting the heat capacity data in the heating of PS and the results for the TNM and AGV models are mutually consistent with each other. The result suggests the existence of such an intermediate aging plateau and the thermodynamic property of which deviates greatly from the extrapolation of the liquid. It is also indicated that both  $T_{gd}$  and  $\delta$  are influenced by molecular weight.

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## 1. Introduction

A nonequilibrium polymer will relax to its thermodynamic equilibrium when it is kept isothermally or heated/cooled. Accompanied with this procedure, the structure and property of the polymer change gradually, which are usually called structure relaxation and physical aging, respectively. The structure relaxation and physical aging of glassy polymers are traditionally important topics in polymer science because of not only their effect on mechanical property but also their relation with the nature of glass transition [1,2].

Whereas, the study on the kinetics of the relaxation is hindered by the fact that the relaxation rate is always very slow especially when the temperature is below glass transition temperature ( $T_g$ ) of the polymer because of the strong decrease of molecular mobility. Various mathematical models have been attempted to describe the relaxation kinetics of materials [3–8], especially on enthalpy relaxation or recovery data determined using a differential scanning calorimetry (DSC). They usually could predict the heat capacity peaks at and even below  $T_g$ , as well as the thermal history dependence of  $T_g$  (or limiting fictive temperature  $T_f$ ) [9–11]. But remarkable thermal history dependence of model parameters, which were assumed to be inherent characteristics of materials, was observed for all the relaxation models. This is the main defects of the present theories and problems faced in this area and no perfect theory or model has been archived hitherto. Simon [12] attributed the case of problems to 3 reasons: (1) the presence of thermal gradients in the sample; (2) an inconsistent equation for describing the

effects of temperature and structure on the relaxation time; or (3) incorrect representation of structural recovery using the Kohlrausch–Williams–Watts (KWW) function.

The temperature gradient in a DSC sample and its effect on the model fitting on experimental heat capacity data have been investigated previously. When a 0.5 mm thick polystyrene (PS) sample was heated at 20 K/min, temperature lag of 1.3 K was obtained by determining the melting point ( $T_m$ ) of indium placed above and below the disk of PS [13]. Significant temperature gradients, amplitudes higher than 2.5 K, were found for PC with 0.6 mm thickness at a heating rate of 20 K/min by Mano and Gómez Ribelles [14]. Through model calculation, Simon reported a maximum temperature lag of 1.2 K for a 1.0 mm poly(ether imide) at a heating rate of 10 K/min [12]. In a previous work, the maximum temperature lag of 1.0 mm thick PS at a heating rate of 10 K/min was calculated to be 0.6 K using an asymmetrical temperature profile model [15]. Nevertheless, it was found that the temperature gradient only has negligible influence on the values of the best-fit model parameters [12,15,16].

The KWW function has received its overwhelming application in the description of structural relaxation [17,18]. Tool–Narayanaswamy–Moynihan (TNM) [3–5] and Adam–Gibbs (AG) [6,7] expressions are the two most commonly used models for describing the effects of temperature and structure on the relaxation time in the KWW function. Another important problem, when one wants to describe the relaxation kinetics, is the thermodynamic property of the material in equilibrium, especially below  $T_g$ . It is closely related to the nature of the glass transition and is still an open topic.

Both the free volume model of Fox and Flory [19] and configuration theory by Gibbs and DiMarzio [20] conceive a characteristic temperature

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of  $T_g$  (or  $T_2$ ), respectively, below which the thermodynamic property of the polymer (volume in free volume model and entropy in configurational entropy theory) deviates from the extrapolations from its liquid. But the TNM model [5–7] and Kovacs–Aklonis–Hutchinson–Ramos (KAHR) model [8] consider the glass transition to be only a kinetic process and no such characteristic temperature exists.

It is assumed implicitly that relaxation in the glassy materials proceeds until the material reaches the extrapolated liquid line when the temperature is higher than  $T_2$  in configurational entropy theory, or in the overall temperature range in the TNM model. Gómez Ribelles [21, 22] introduced a limit state concept that the equilibrium configurational entropy deviates from configurational entropy of the extrapolated liquid line far above  $T_2$ . The heat capacity difference between the limit state and the extrapolation from the liquid line,  $\delta_{GR}$ , was determined upon a curve fitting approach that minimizes the standard deviation between the experimental and calculated normalized heat capacity data. Other researchers [23–27] also showed that the recovered enthalpy appears to reach a plateau, which corresponds to an enthalpy level considerably higher than that obtained by extrapolating from the liquid data above  $T_g$ .

Hutchinson [28] and Simon [29,30] criticized the existence of such a limit state or aging plateau. They suggested that the liquid enthalpy line is reached at temperatures below  $T_g$ . The enthalpy loss data of PS at 358 K of Koh and Simon [30] only deviate from the data of Cangialosi et al. [31] after the logarithmic aging times of approximately 5.5. Recently, double-step enthalpy recovery at relatively low aging temperatures was found, which indicates the presence of two time scales of equilibration [32]. The first decay was tentatively attributed to the secondary relaxations based on the relatively low activation energy. The equilibration time to the second plateau is much longer than the first plateau in orders. Cangialosi considered that polymer  $\alpha$  process is responsible for the second decay based on the fact that the adequate description of the temperature dependence of the equilibration time using the same VFT law employed to fit dielectric relaxation data above  $T_g$ . Whereas a fact should be noticed is that the free volume changes with temperature above  $T_g$  but be frozen below  $T_g$ . This indicates that the temperature dependence of relaxation time of  $\alpha$  process may be changed [33]. It is also worthwhile to notice that a 2-step recovery after plastic deformation has also been reported in the case of several polymers, such as PS, PMMA and BPA-PC [34]: one releases energy and recovers volume below  $T_g$  and the other releases energy and recovers dimension above  $T_g$ . The fast process is attributed to short range atomic/molecular rearrangement while the slow process exhibits a cooperative character. Nevertheless, the mechanism of the fast and slow aging processes below  $T_g$  is still unclear to our knowledge.

In this paper, the first aging plateau is described by  $T_{gd}$  and  $\delta$ . The evolution of the second step of enthalpy recovery is neglected due to its large scales of relaxation time [32]. The enthalpy recovery of PS is restudied by investigating the heat capacity data based on the new model. We hope that the enthalpy relaxation could be described more accurately and validate the existence of such an intermediate aging plateau from curve fitting of heat capacity data.

## 2. Experiments and methodology

### 2.1. Samples and DSC measurements

The PS samples (labeled as PS4K, PS50K and PS152K) with Mw of 4.0, 50.0 and 152.0 kDa and narrow molecular weight distributions (polydispersity index (Mw/Mn) smaller than 1.06) were purchased from Tianjin Alfa Aesar Chem Corp. A Perkin-Elmer Diamond DSC was used in this study. The DSC was calibrated with high purity indium. Accurately weighted PS sample (about 5 mg) was put into the aluminum DSC pan and then covered with an aluminum lid. It was heated to 423.15 K on a Linkam THMS600 hotstage and the lid was pressed carefully to assure that the polymer to be molded to a cylinder with uniform

thickness contacts with the pan bottom and the lid tightly. The thicknesses of the samples were determined with a micrometer and closes to that calculated from the sample weight, density and the DSC pan diameter. The DSC pan was sealed carefully not changing the lid detectably to assure that the contact of the sample with the pan and lid does not change. All the determinations were carried out under nitrogen atmosphere.

The sample was first heated to a temperature far above  $T_g$  (423.15 K) at a heating rate of 10 K/min and kept in the calorimeter cell isothermally for 5 min to erase the thermal history memory. Then it was cooled to a temperature far below  $T_g$  (273.15 K) at one of four available constant cooling rates (100, 10, 1 and 0.1 K/min). Subsequently, the sample was reheated immediately to the initial temperature at 10 K/min. For the case of annealing time investigation, the cooling rate was fixed at 10 K/min, while during the cooling course it was annealed for a time  $t_a$  (0, 2, 10, 60, 300 and 1200 min) at a certain annealing temperature  $T_a$  (343.15 K for PS4K, 363.15 K for PS50K and 365.15 K for PS152K). Only the signal in heating scan was recorded and analyzed. The data recording interval was fixed at 1 s.

The experimental normalized heat capacity,  $C_{p,exp}^N$ , was obtained by its definition:

$$C_{p,exp}^N = \frac{C_p(T) - C_{pg}(T)}{C_{pl}(T) - C_{pg}(T)} \quad (1)$$

where  $C_p$ ,  $C_{pg}$  and  $C_{pl}$  are isobaric heat capacities of the sample, glass and liquid (rubber), respectively.  $C_{pg}$  and  $C_{pl}$  were obtained by linear extrapolation from the glassy and rubbery states.

### 2.2. Calculation and model fitting

The evolution of structure of PS during relaxation is described with  $T_f$  at any temperature (time) which is calculated by combining Boltzmann superposition principle with the KWW function:

$$T_f(T) = T_i + \int_{T_i}^T \left\{ 1 - \exp \left[ - \left( \int_{t(T)}^{t(T)} \frac{1}{\tau} dt \right)^{\beta} \right] \right\} dT_d \quad (2)$$

where  $T_i$  is the initial temperature far above  $T_g$  in the DSC measurement where the polymer is in the equilibrium liquid state and  $T_f$  coincides with the temperature  $T$ .

The relaxation time  $\tau$  in Eq. (2) is calculated using both the widely used phenomenological TNM equation and Adam–Gibbs–Vogel (AGV) equation based on Adam and Gibbs' approach to investigate the influence of relaxation time model on the result. The TNM equation describes the dependence of  $\tau$  on temperature and the degree of departure from equilibrium as:

$$\tau = A \exp \left[ \frac{x\Delta h}{RT} + \frac{(1-x)\Delta h}{RT_f} \right] \quad (3)$$

where  $A$  is the pre-exponential factor,  $\Delta h$  is the apparent energy for structural relaxation,  $x$  ( $0 < x \leq 1$ ) is the nonlinearity parameter, and  $R$  is the gas constant.

The AGV equation was introduced by Hodge [7] as a theoretical basis for treating nonlinearity expressed as:

$$\tau = A \exp \left[ \frac{D}{T \left( 1 - \frac{T_2}{T_f} \right)} \right] \quad (4)$$

The AGV equation has its superiority over other expressions of assuming the form of Vogel [35] and Williams–Landel–Ferry (WLF) [36] equations in the equilibrium state ( $T_f = T$ ).

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