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# Enthalpy relaxation of polystyrene at different molecular weight using fast calorimetry

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## Abstract

The enthalpy recovery of polystyrene materials with narrow molecular weight distribution is studied by means of fast calorimetry. Two different molecular weights, Mw, have been investigated, namely 2000K and 212k. Intrinsic isotherm experiments at aging temperatures ranging from above to below the nominal Tg have been reported. The effect of the cooling rate on the glass transition temperature is also exanimated and it is showed that the cooling rate-dependence of the Tg is Vogel-Fulcher and not Arrhenius. The main finding is that the enthalpy recovery kinetics is not affected by the molecular weight showing that the contribution to free volume related due to chain terminals is negligible in the molecular weight range (212k-2000k) analysed in this paper.

*Keywords:* glass transition; structural recovery; relaxation; polystyrene; fast calorimetry

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## 1. Introduction

When a glass is cooled from the melt state at a temperature below the $T_g$, its structure-sensitive properties, such as volume and enthalpy, deviate from the equilibrium and reach a non-stable thermodynamic state. Under isothermal condition, it's possible to observe a spontaneous and time dependent evolution of each property toward a stable thermodynamic state. This phenomenology is usually referred to as structural recovery or physical aging [1-8].

The polymer chains, subjected to a sudden variation in temperature, aren't fast enough to rearrange instantly to the lowest energy configuration and in most cases are far away from that. This kinetic can be directly evaluated by differential scanning calorimetry. If a polymer is reheated at the melt state after a sudden cooling, its calorimetric curve will show a well-defined peak around its glass transition temperature. The peak is higher as long as the chain

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configuration is approaching the equilibrium. During physical aging, polymers evolve toward a more thermodynamic stable condition. Short aging times are directly correlated to low and wide peaks while long aging times to high and narrow peaks. Cooling rate is another important element to consider, namely: the slower the change in temperature the more the time available for chains to rearrange. Quick cooling will determine very instable configurations and consequently high and narrow calorimetric peaks.

In this study, the material response was monitored using rapid scanning calorimetry (flash-DSC), that allowed to reach very high cooling rates (up to 1000K/s) and to determine enthalpy changes for very short aging times (from 0.01s). Conventional differential scanning calorimetry (conventional-DSC) is unable to determine accurately such small enthalpy changes due to the limited performances in terms of heating/cooling rates. This approach enables to overcome these limitations and consider aging temperatures even 10-15°C above the nominal $T_g$.

## 2. Experimental

The polystyrene samples under study were provided by Sigma-Aldrich and have molecular weights ($M_w$) of 212,000 g/mol and 2,000,000 g/mol. Experiments were performed with a commercial rapid-scanning calorimeter, the Mettler Toledo Flash DSC, purged with nitrogen at a constant flow rate of 20 mL/min. Bulk samples were cut with a microtome to obtain a square shape of dimension of approximately 150 $\mu m^2$ and then arranged on the flash-DSC chip.

In this paper both the effects of aging and cooling rate were investigated. Experimentally, this can be done submitting the sample material to appropriate thermal histories. All the temperature cycles used for aging experiments begin by heating to 190°C and holding the temperature constant for 6s. This is necessary to erase the effect of any previous thermal history and bring the sample in equilibrium. That temperature is far above the $T_g$ of polystyrene of any molecular weight and is sufficient to determine the complete relaxation of the polymer, avoiding degradation at the same time. As showed in Fig. 1(a), the sample was then cooled to different aging temperatures $T_a$ and aged for times ($t_a$) ranging from 0.012s to 60000s. The aged sample was then cooled to room temperature (30°C) and then reheated at 190°C to evaluate the calorimetric peak. In all cases cooling and heating rates are fixed to 1000K/s. Each experiment considered a different aging temperature. For the 2,000,000 g/mol polystyrene six different $T_a$ were considered: 82.5°C, 92.5°C, 102.5°C, 106.5°C, 109.5°C, 112.5°C. The 212,000 g/mol polystyrene was also evaluated at the following $T_a$: 99.5°C, 105.5°C, 108.5°C, 111.5°C, 114°C. The investigation of the effect of cooling rate on glass transition requires a slightly different temperature cycles: after erasing thermal history, the sample was cooled to room temperature (30°C) at different rates ($q$ = 0.1K/s, 1K/s, 10K/s, 100K/s, 1000K/s) and then reheated to 190°C at 1000K/s to evaluate the calorimetric peak. It's basically the same experiment showed in Fig. 1(a) but without aging and with different cooling rates $q$.

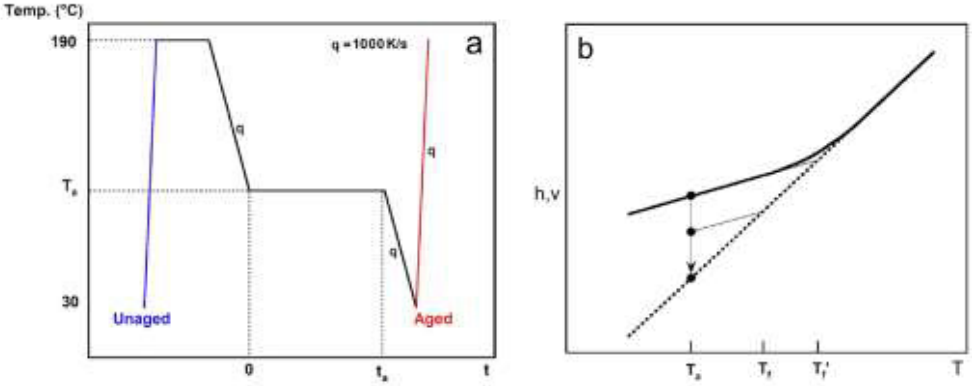

Fig. 1. (a) schematic diagram of the thermal histories executed on the flash DSC to study structural recovery of polystyrene; (b) correlation between fictive temperature ($T_f$) and structure-sensitive properties (enthalpy and volume) during aging experiments.