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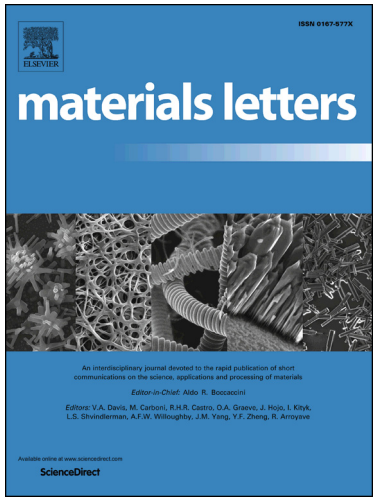

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Chirality impact on physical ageing: an original case of a small organic molecule

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Abstract:

The purpose of this paper is to investigate the structural relaxation of N-acetyl-α-methylbenzylamine (Nac-MBA), a chiral organic molecule, through the study of the glass transition temperature T_g and the well-known physical ageing, occuring at temperatures lower than T_g. The influence of the enantiomeric excess (ee) on the structural relaxation kinetics is highlighted through standard differential scanning calorimetry (DSC) and Fast Scanning Calorimetry (FSC) investigations. This original work evidences that even if the enthalpy loss to reach equilibrium remains globally the same whatever the ee, the structural relaxation kinetics are clearly slowed down when ee is increased.

Keywords: Organic compounds, physical ageing, Differential Scanning Calorimetry, Fast Scanning Calorimetry, Chirality

Introduction:

The physical ageing is a well-known natural phenomenon occurring when a glass is maintained during a certain time below its glass transition temperature. The thermal signature of this physical phenomenon (corresponding to an endothermic peak) is more or less intensive, depending on the ageing duration t_a and on the gap between the glass transition temperature T_g and the temperature at which the glass is maintained T_a. Using physical aging signature to reveal the thermal history and the thermal stability of a glass is a common procedure as proven by the recent literature on this topic **[1–5]**. Furthermore, knowing the physical ageing process is essential for predicting the time-dependent behavior of glassy systems, particularly if they are used under their glass transition temperature for a long time**.** One of the main relevant parameter related to the physical ageing is the enthalpy loss calculated by integrating the difference between the scans of aged and rejuvenated sample according to the following equation:

$$\Delta H(T_a,t_a) = \int_{T_1}^{T_2} \left[C_p^a(T) - C_p^r(T)\right].dT \qquad (1)$$

in which $C_p^a(T)$ and $C_p^r(T)$ are the specific heat of aged and rejuvenated samples respectively, and T_1 and T_2 are arbitrary temperatures below and above T_g. Under the assumption that thermodynamic equilibrium is reached for an infinite aging time, the expected enthalpy loss ΔH_∞ extrapolated from the equilibrium melt depends on T_a, T_g and on the heat capacity step ΔC_p of the sample, according to the following relation:

$$\Delta H_\infty = \Delta C_p.\left(T_g - T_a\right) \qquad (2)$$

Reaching or not the equilibrium state after a very long ageing time duration is still matter of debate in the scientific community **[6–11]**. Andreozzi et al. **[12]** explained that the equilibrium state cannot be reached in the case of high molecular weight PMMA because of the chain entanglement. The influence of chain entanglement and steric hindrance on the enthalpy loss is also the hypothesis used in the entropic model proposed by J.L. Gomez Ribelles to explain that the equilibrium state cannot be reached **[13]**. However, using the Fast Scanning Calorimetry (FSC) has proven the possibility to reach the equilibrium state in acceptable times on the experimental scale **[14–17]**. This phenomenon is clearly explained by the fact that FSC investigations accelerate the kinetics of physical aging.

The aim of this work is to investigate the structural relaxation of N-acetyl-α-methylbenzylamine (Nac-MBA), a chiral organic compound derivative from α-methylbenzylamine (a widely used chiral resolving agent for optical resolution **[18])**, through the study of T_g and the physical ageing process. In the specific case of the Nac-MBA, the enantiomeric excess (i.e. the absolute difference between the mole fractions of each enantiomer, noted ee) influence on the structural relaxation kinetics have been highlighted.

Materials and methods:

Materials

Optically pure and racemic Nac-MBA were synthesized by acetylation of α-methylbenzylamine purchased from Aldrich (99%) using either acetic anhydride or acetyl chloride (for more details see supplementary information: Materials). Samples of

several ee were prepared by physical mixtures of both enantiomers. For example, an ee = 0% contains the same amount of both enantiomers (i.e. racemic), when an ee = 100 % is enantiomerically pure.

Differential Scanning Calorimetry analysis

DSC experiments were launched with a Perkin Elmer 8500. Cooling was ensured by a refrigerated cooling system (IntraCooler II). The temperature and enthalpy calibrations were achieved using indium and benzophenone as reference materials. Measurements were performed with 5mg of material under nitrogen gas flow. Ageing was performed 5 °C below T_g for different ageing duration t_a (from 1 to 720 min) after a rejuvenation cycle (sample heated above T_g and cooled down to T_a at 20°C/min). After the isothermal ageing, the sample is cooled below T_a, i.e. -70°C, at 20°C/min, and heated at the same rate above T_g, in regards to record the aged glass signal. The same cycle is repeated to record the unaged glass signal.

Fast scanning calorimetric measurements

FSC analyses were performed using a power compensation twin-type chip-based fast scanning calorimeter Flash DSC 1 (Mettler Toledo) equipped with a Huber TC100 intra-cooler. The specific calibration procedure for this tool is detailed in ref **[17]**. The samples were placed on the sensitive area of a MultiSTAR UFS 1 MEMS chip sensor. A thin layer of silicone oil has been used, promoting adhesion of the sample onto the chip and improving thermal contact. Samples were continuously flushed with a gaseous nitrogen flow. Sample masses (few ten nanograms) were estimated by normalizing the heat capacity jump at T_g with the value obtained from classical DSC measurements. As well explained in ref **[17]** it is not easy to perfectly master the ee value during sample preparation for FSC experiments. Ageing was performed 6 °C below T_g for different

ageing duration t_a (0.01 s to 14400s) after a rejuvenation cycle (sample heated above T_g and at 1000°C/s down to T_a). After the isothermal ageing, the sample is cooled below T_a, i.e. -70°C, at 1000 °C/s, and heated at 1000 °C/s above T_g to record the aged glass signal. The same cycle is repeated to record the unaged glass signal.

Results and discussion:

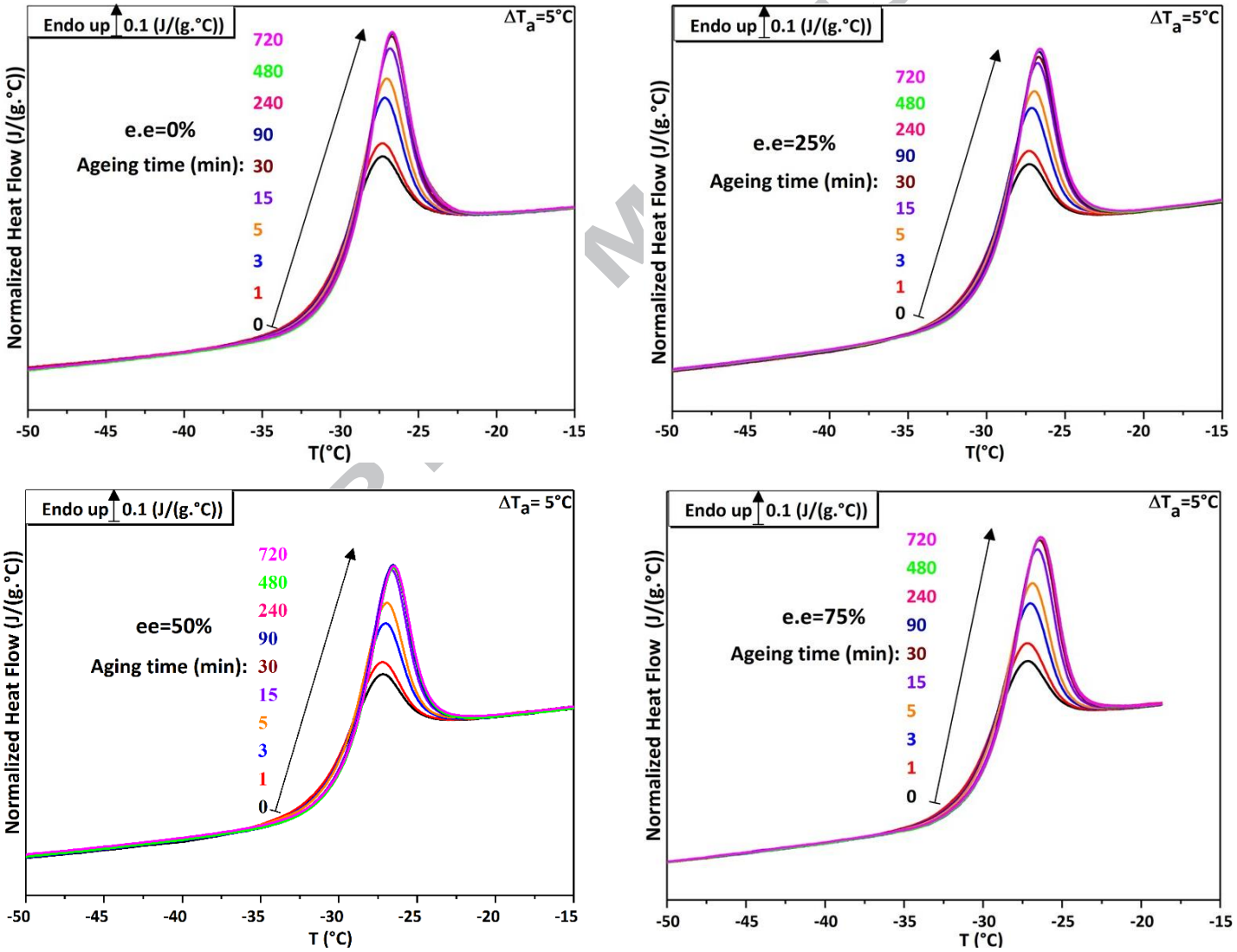

Figure 1 : DSC experiments: Normalized Heat Flow curves recorded during heating ramps after isothermal ageing as a function of ee%. $\Delta T_a = (T_g - T_a) = 5°C$ with T_g = -32

± 0.5°C.

Figure 1 shows normalized heat flow curves recorded during heating ramps from DSC experiments. Expected behavior is obtained, i.e. an endothermic peak superimposed to the heat capacity step at T_g, with an increasing amplitude and shifting towards higher temperatures when the ageing duration increasing from 0 up to 720 min. Whatever the enentiomeric excess, the same behavior is observed.

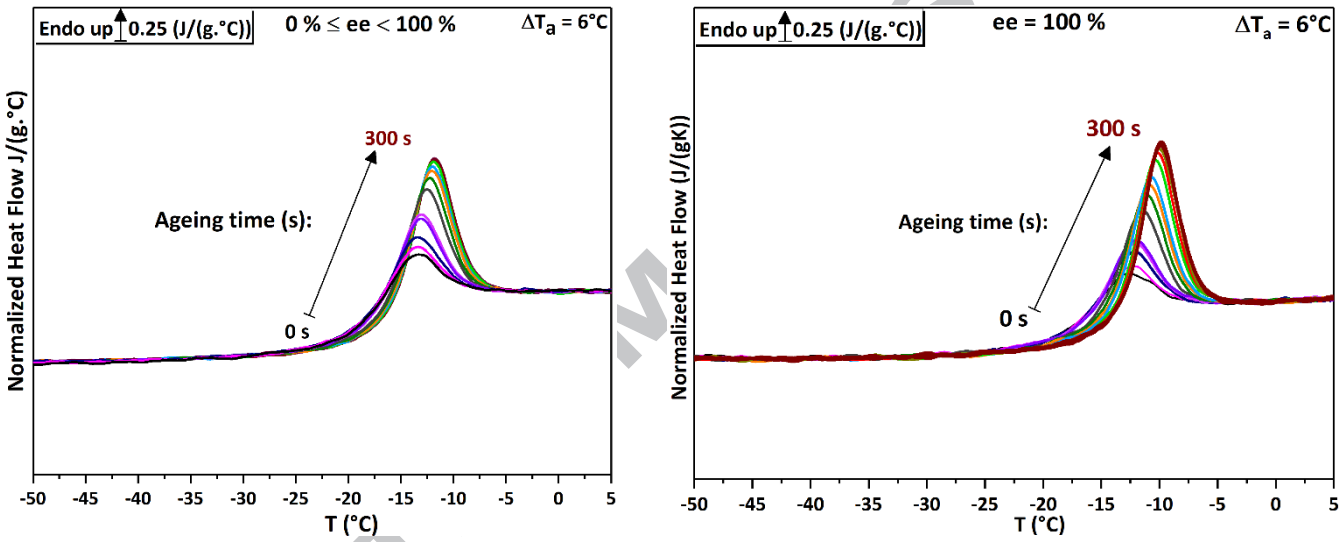

Figure 2: FSC experiments: Normalized heat flow curves recorded after physical ageing during heating ramps as a function of ee%. $\Delta T_a = (T_g - T_a) = 6°C$ with $T_g = -22 \pm 0.5°C$

Figure 2 shows FSC curves obtained after in-situ ageing performed at $T_a = T_g - 6°C$. As ageing duration increases, the endothermic peaks superimposed to heat capacity step at T_g are shifted towards high temperatures with an increasing magnitude as expected. We may note that the glass transition zone shifting in comparison to DSC experiments is classically observed from FSC experiments due to the very high heating rate used.

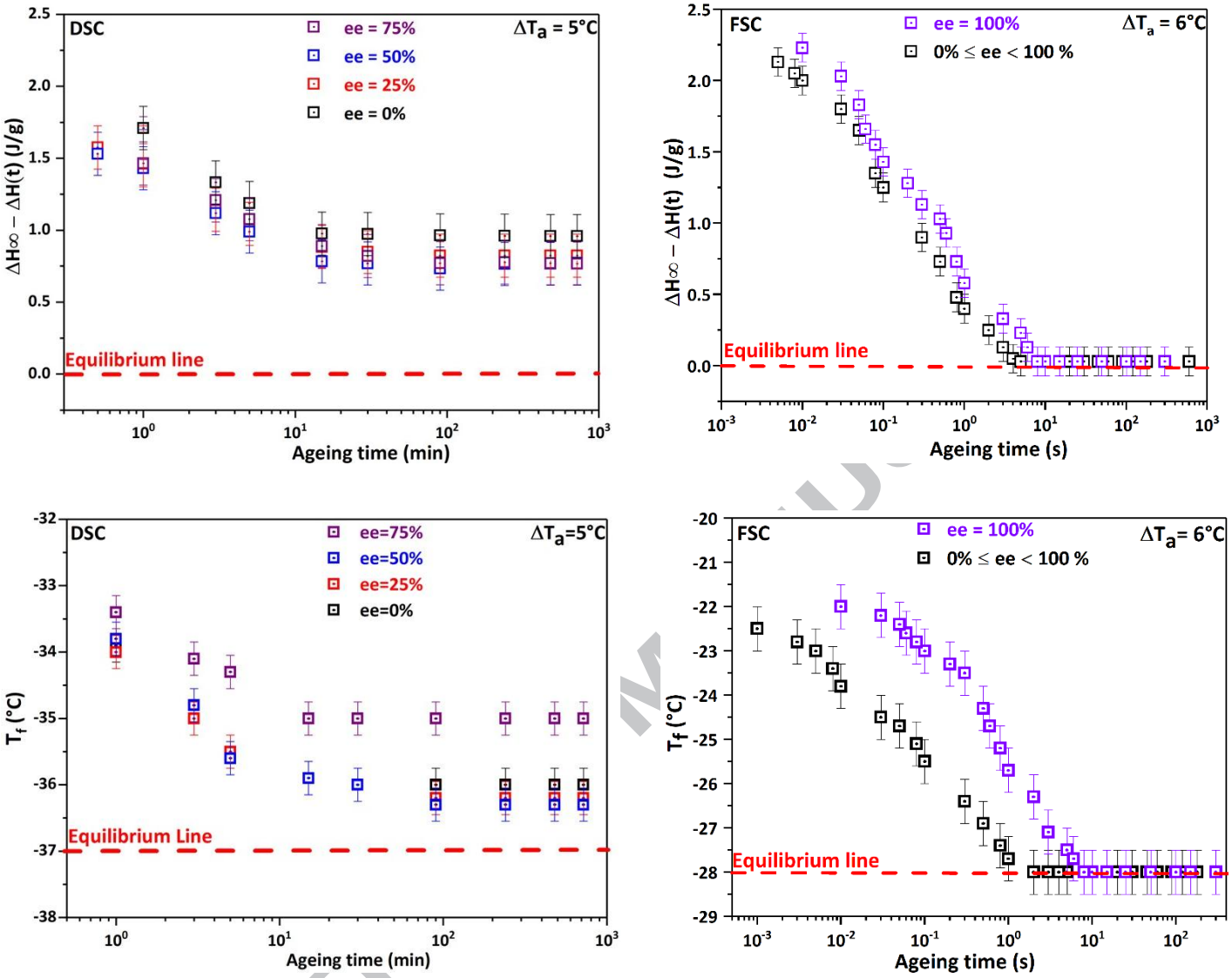

Figure 3: FSC and DSC experiments. On the top: Time evolution of the difference between ΔH_∞ and ΔH_t for the aged samples in function of ee. On the bottom: Time evolution of the fictive temperature in function of ee.

Figure 3 (top) gives the evolution of the difference between the ΔH_∞ calculated from equation 2 and ΔH_t depending on the ageing duration calculated from equation 1. Concerning the reaching of equilibrium state, a clear difference is observed between the experiments performed by DSC (left) and those performed by FSC (right): as expected, FSC experiments allow reaching the equilibrium line as explained in literature **[14–17]**. Unfortunately, according to the error bars it is not possible to highlight a tendency

concerning the ee influence on the enthalpy loss. Figure 3 (bottom) shows the time evolution of the fictive temperature T_f in function of ee. The T_f concept has been introduced by Tool in 1931 and defines the temperature at which any properties, related to the structural relaxation, are at the equilibrium state **[19, 20]**. T_f is calculated from the heating curves using the ''equal area rule'' method **[20]**. According to this concept, the equilibrium state is reached when T_f is equal to T_a. This allows us to confirm that FSC experiments are consistent since T_f = -28°C = T_g - 6°C at the equilibrium state as shown in figure 3 (bottom – right). Concerning the influence of ee, we observe in figure 3(bottom-right) that, for a same ageing duration t_a, the gap between T_f and the equilibrium line is greater for ee = 100% than for 0 < ee < 100%. Thus, the ee seems to slow down the structural relaxation kinetics during the physical ageing. Thus, we can conclude that the enthalpy loss needed to reach the equilibrium does not depends on ee (similar variations in terms of gap between ΔH_∞ and ΔH_t), but the velocity to reach this equilibrium is ee dependent.

Conclusion

The physical ageing process of N-acetyl-α-methylbenzylamine (Nac-MBA) was investigated by thermal analyses. Through FSC investigations, we have shown that the equilibrium state can be reached even if it seemed not possible from DSC investigations. Furthermore, as far as we know, this is the first study highlighting that: i) as expected (Tg and ΔC_P being ee independent) the enthalpy loss needed to reach the equilibrium for a chiral amorphous glass is independent from the enantiomeric excess (ee), whereas ii) the velocity to reach this equilibrium is ee dependent.

Acknowledgments

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Highlights:

- Physical ageing of chiral N-acetyl-α-methylbenzylamine studied by DSC and FSC.

- Influence of the enantiomeric excess (ee) is highlighted.
- Accelerated aging kinetics are observed from FSC analysis.
- The enthalpy recovery to reach the equilibrium is ee independent.
- The velocity to reach the equilibrium is ee dependent.