The consequence of excess configurational entropy on fragility: the case of a polymer/oligomer blend

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Abstract

By taking advantage of the molecular weight dependence of the glass transition of polymers and their ability to form perfectly miscible blends, we propose a way to modify the fragility of a system, from fragile to strong, keeping the same glass properties, i.e. vibrational density of states, mean-square displacement and local structure. Both slow and fast dynamics are investigated by calorimetry and neutron scattering in an athermal polystyrene/oligomer blend, and compared to those of a pure 17-mer polystyrene considered to be a reference, of same \(T_g\). Whereas the blend and the pure 17-mer have the same heat capacity in the glass and in the liquid, their fragilities differ strongly. This difference in fragility is related to an extra configurational entropy created by the mixing process and acting at a scale much larger than the interchain distance, without affecting the fast dynamics and the structure of the glass.
The origin of the dramatic slowing down of dynamics in molecular liquid and polymer on the approach to the glass transition is still a hotly debated question in condensed matter physics. Viscosity and relaxation time show an increase of more than ten orders of magnitude while temperature decreases by a few tens of degrees. It comes with a rapid decrease of the configurational entropy defined as the excess entropy of the metastable liquid over the crystal (as suggested by Adam and Gibbs [1]), supporting the hypothesis of an underlying thermodynamic transition. The relaxation time $\tau_\alpha$ shows different temperature dependences in different systems, that can be quantified at the glass transition temperature $T_g$ via the isobaric fragility, introduced by Angell [2]

$$m_P = \left( \frac{\partial \log_{10}(\tau_\alpha/\tau_0)}{\partial T/T_g} \right)_{T=T_g},$$

with $\tau_0=1s$. The fragility values range from 20 for so-called strong systems such as silica to more than 200 for some fragile polymeric systems. The classification of systems according to this index arose from an attempt to understand the universal slowing down and the glass formation itself. It is however difficult to extract a generic description by comparing chemically very different systems that as a result show quite specific relaxation behavior. Various methods have been proposed in the literature to maintain constant intermolecular interactions while changing other properties such as fragility. For example, a single molecular liquid or polymer may be studied at different pressures, thereby changing the glass transition in the same chemical system [4]. Another very effective way to tune fragility without changing the chemistry is to vary the chain length of a polymer. This affects $T_g$, $m_P$, heat capacity jump, density, mean-square displacement (MSD), Boson peak (BP) and other properties related to the glass transition [4, 5]. We propose here a third approach, changing polydispersity $I_p$. We mix a high molecular weight $M_n$ polystyrene (PS) with its oligomer creating an athermal polymer/oligomer blend and compare its behavior with a monodisperse reference sample of exactly same $T_g$ as the blend. These two samples are very similar at the local scale, as will be shown from structural measurements in this Letter. Having such similar samples can only be achieved using polymers of the same chemical nature. Thanks to the effect of $M_n$ on their physical properties, the reference of a pure system such as the 17-mer is available while it is not in the usual polymer-polymer or molecular liquids mixtures that have been extensively studied in the literature [6, 7, 8, 9, 10, 11] for other purposes. A comparative study of these two samples is an ideal way to better understand fragility while minimally affecting the system. We present here an extensive study of their thermodynamics,
structure and slow and fast dynamics.

Differential scanning calorimetry and elastic and inelastic neutron scattering are used to measure the heat capacity, the structure factor $S(Q)$, the MSD at the nanosecond timescale and the BP in the blend and in the 17-mer. We have focused on the structure and dynamics at the local scale corresponding to the usual wave vectors range studied for glass transition, from 0.5 to 2 Å$^{-1}$. We have found that neither thermodynamics nor local structure nor fast dynamics and vibrations differ in the two samples, although the fragility is quite different. We propose to rationalize this difference in fragility via an excess configurational entropy of the polymer/oligomer blend compared to the monodisperse sample, and to establish a direct link between these two quantities at a lengthscale much larger than the interchain distance.

Narrow $M_n$ distribution polystyrene samples (hydrogenated, labeled $h$, and deuterated, $d$) were purchased from Polymer Standards Service. All sample characteristics are summarized in table I. A bimodal polystyrene blend has been prepared with 62% by weight of PSh92k and 38% of PSh750) thus obtaining the same $T_g$ as for the PSh1790. A fully deuterated blend (62% PSd110k and 38% PSd800) has also been prepared as well as the corresponding pure sample PSd2300. Calorimetry experiments have been performed on the blend and on its pure components, leading to the conclusion that the PS/oligomer blend is athermal, i.e. shows no enthalpy of mixing, consistent with results on similar systems [12, 13]. The measurements were performed on a Mettler Toledo DSC by cooling from above the nominal $T_g$ at different rates ranging from 0.03 to 30 K.min$^{-1}$ followed by a heating scan at 10 K.min$^{-1}$. The limiting fictive temperature $T'_f$, which is equivalent to $T_g$ and defined as the intercept of the extrapolated liquid and glass lines obtained on heating [14], was calculated using the instrumental software. All of the neutron scattering experiments were realized using hollow cylindrical aluminium cells containing a film of the sample wrapped in an aluminium foil. The films were prepared under vacuum with a thickness corresponding to a 10% scattering of the incident beam. Inelastic neutron scattering measurements were performed on PSh1790 and the fully hydrogenated blend using the time-of-flight instrument Mibémol at the Laboratoire Leon Brillouin (Saclay, France), at an incoming wavelength of 6 Å and a Full Width Half Maximum (FWHM) resolution around 100 µeV. The Q-range for this setup is 0.45 to 1.95 Å$^{-1}$. The data were corrected for detector efficiency, background container scattering, and self-shielding us-
ing a standard procedure. The Backscattering Neutron measurements were carried out on IN16 at the Institut Laue-Langevin (Grenoble, France). The temperature scans have been measured between 2K and 480K at a wavelength of 6.27 Å and the Q ranges from 0.2 to 1.9 Å\(^{-1}\). The data were corrected for detector efficiency, sample container scattering and self-shielding by the standard programs. The mean-square displacement is determined from the observed elastic scattering \(I_{el}\) with a resolution \(FWHM = 0.85 \mu eV (4\) ns) which is an average over all scattering atoms weighted by their cross section. Within the incoherent Gaussian approximation the effective MSD (relative to the frozen state) can be deduced from the slope of \(\ln(I_{el}/I_{el}(2K))\) versus \(Q^2\). The deduced MSD arises for hPS to nearly 92% from incoherent scattering of the protons. We measured the partially deuterated blend sample, where the scattering is dominated (75%) by the scattering of the protons, and expect a similar result to that of a totally hydrogenated blend. The structural characterization of the blends and pure components have been performed on the D7 spectrometer (ILL) in its diffraction mode, using deuterated samples to get the coherent information. The incoming wavelength was 4.8 Å and the investigated Q-range: 0.2 Å\(^{-1}\) to 2.75 Å\(^{-1}\).

| Samples         | Mn (kg/mol\(^{-1}\)) | \(I_p=Mw/Mn\) | \(T_g\) (K) | \(m_p\) |
|-----------------|------------------------|----------------|-------------|---------|
| PSh92k          | 92                     | 1.04           | 373.1 ± 0.4 | 180 ± 13|
| PSh1790         | 1.79                   | 1.06           | 325.7 ± 0.2 | 109 ± 7 |
| PSh750          | 0.735                  | 1.08           | 276.0 ± 0.2 | 113 ± 5 |
| PSh92k/PSh750   | 1.91                   | 31.3           | 325.6 ± 0.8 | 85 ± 6  |
| Psd110k/PSh750  | 1.91                   | 36.1           | 324.7 ± 0.9 | 86 ± 7  |
| Psd110k/Psd800  | 2.04                   | 33.87          | 325.3 ± 0.8 | 89 ± 7  |
| Psd110k         | 109                    | 1.02           | 372.7 ± 0.4 | 149 ± 10|
| Psd2300         | 2.21                   | 1.049          | 336.6 ± 0.4 | 129 ± 3 |
| Psd800          | 0.785                  | 1.10           | 277.5 ± 0.2 | 96 ± 4  |

TABLE I: Sample description and characteristics

Figure I shows that the blend and PSh1790 have the same glass transition temperature and absolute heat capacity as measured by step scan experiments, both deep in the glass
and in the liquid state. In the first inset, however, the normalized heat capacity measured on heating shows a different broadening of the glass transition and aging effects, illustrating that their slow dynamics differs. The difference in fragility and apparent activation energy is evidenced by the different dependences of the limiting fictive temperatures on cooling rate \cite{15}, shown in the second inset. The fragility obtained for the blend is 20\% lower ($m_P=85$) than for the monodisperse PSh1790, $m_P=109$, which is consistent with previous ones \cite{8,16} on other PS blends. Moreover the blend fragility is closer to that of its low $M_w$ component and much stronger than the high $M_w$ component. By fitting the $C_p$ curves with the Tool-Narayanaswamy-Moynihan model \cite{17} of structural recovery, we extracted a Kohlraush stretching exponent $\beta_{KWW}$ for the blend of 0.4 lower than for the 17-mer, of approximatively 0.7, consistent with the obvious fact that blending broadens

FIG. 1: Absolute heat capacity versus temperature. Monodisperse PSh1790 (stars) and bidisperse blend PSh92k/h750 (crosses) of same $T_g$. First inset: Apparent $C_p$ versus T measured by DSC on heating at 10K.min$^{-1}$ after cooling at 10K.min$^{-1}$. Second inset: $T_f'$ versus logarithm of cooling rate. [View in color for better clarity].

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the distribution of relaxation times. Thus, we have a polymer/oligomer blend with a lower fragility and a lower $\beta_{KW}$ than the reference monodisperse sample; on the other hand, a decrease in fragility is usually accompanied with an increase in $\beta_{KW}$ in pure molecular liquids and polymers [9, 10]. In his work on a polydisperse high molecular weight PS, Privalko [16] found close results but he explained it by a change in the local PS structure. Our results do not support such structural changes as can be seen in figure 2. It shows the structure factor for deuterated samples at 100K. Two main peaks are observed: the first one near $5 \text{ nm}^{-1}$ corresponds to the typical interchain distance (involving C and D chain-chain correlations), whereas the second around $13-14 \text{ nm}^{-1}$ corresponds to the distance between phenyl groups (phenyl-phenyl correlations), as is well known from literature [18, 19]. The structure factors of the blend and of the pure 17-mer PS of same $T_g$ are very similar, especially when compared to the more significant changes produced by the molecular weight on the pure components of the blend. The local density of the blend seems to be well predicted by a simple sum rule from the pure components local densities which confirms the ideal character of our blend. The interchain lengthscale corresponds to the static lengthscale at which the signature of the glass transition is observed, as shown from the temperature dependence of the first diffraction peak [3, 20] or from the change in the temperature-dependence of the MSD. At the same local scale, the mobility of the atoms can be measured by neutron backscattering technique via the mean-square displacement averaged over all the atoms at the ns scale. The upturn in the temperature dependence coincides with the macroscopic $T_g$, even though the resolution of the experiments is 4ns. In figure 3, we show the MSD of the blend and some pure PS over a wide temperature range. MSD of the blend and the 17-mer coincide but are distinct from those of the pure components of the blend due to their differences in $T_g$. Starting from the correlation between the location of the upturn of the MSD and $T_g$, the temperature dependence of the MSD around $T_g$ has been correlated to the fragility in [21, 22]. We do not observe the correlation here: the slope is the same for the blend and the 17-mer, as can be seen from the inset of figure 3.

Another correlation between fast and slow dynamics discussed in the literature relates the strength of the quasielastic scattering intensity at $T_g$ (normalized to the intensity of the boson peak as measured by inelastic scattering) and the fragility [23]. For both the blend and the 17-mer, the dynamic structure factor is plotted in figure 4 at 100K from TOF
FIG. 2: Structure factor of the samples from the coherent signal of the deuterated samples at 100K. The pure components of the blend are also shown to illustrate the \( M_n \) dependence of the structure.

neutron scattering experiments: they have superimposable boson peaks implying similar vibrational density of states (VDOS) consistent with the very low temperature MSD (figure 3) and heat capacity measurements (inset of 4). Only a very small difference in the quasi-elastic scattering region may be seen, which is however five times lower than the change observed with molecular weight (not shown on the figure for reasons of clarity) and could be attributed here to the thermal treatment we imposed: another experiment performed on the blend under a rapid quench leads to almost identical spectra.

One may then wonder what causes the difference in the slow dynamics, \textit{i.e.} fragility and apparent activation energy of the two systems. The miscibility of both components in the athermal polymer/oligomer blend is not enthalpy driven here and must be accompanied by an increase of entropy. We suggest that a change in configurational entropy due to mixing is at the origin of the observed change in the fragility. From recent arguments proposed in the literature \([24, 25]\), the entropy of mixing is related to the difference
FIG. 3: MSD at the ns timescale of the pure components and the blend. Inset: rescaled data, \( \frac{\langle u^2 \rangle}{\langle u^2 \rangle_g} \) versus \( T/T_g \).

between the \( T_g \) of the blend calculated by using simple additivity rules and the measured value. Indeed, we had to prepare a blend containing 6% less chain ends than in the monodisperse PSh1790 in order to have the same \( T_g \) (it is usually known in polymeric mixtures that one cannot relate directly the \( T_g \) to the number of chain ends as it is usually done for monodisperse polymers). The extra mixing contribution to the configurational entropy can be estimated from recent work \[24\] and is found to be rather small as compared to the polymer configurational entropy at \( T_g \). However, Pinal \[24\] also points out that the cooling rate dependence of \( T_g \) for mixtures implies a cooling rate dependent entropy, which in turns may be related to the fragility difference between blend and pure PS.

By taking advantage of polymer molecular weight dependent properties, we have been able to build a model system that show direct connection between the slow dynamics and an excess configurational entropy acting at lengthscales much larger than the intermolecular (interchain) distance. Two samples of same \( T_g \): an athermal polystyrene/oligomer blend and a reference monodisperse polystyrene sample were
FIG. 4: Dynamic structure factor of the blend and the 17-mer PS at 100K. Inset: low temperature \(C_p\) values for both systems measured by calorimetry.

used. They are exactly equivalent at their local scale, as demonstrated from their structural arrangements and their fast dynamics and vibrational processes, whereas their slow dynamics, quantified by the fragilities, are significantly different. We suggest to rationalize this difference in fragility via an excess configurational entropy of the polymer/oligomer blend and establish a direct link between these two quantities. Moreover we have provided evidence that the origin of the very high fragility of polymers as compared to molecular liquids involves structural features occurring at a lengthscale much larger than the interchain or intermolecular distance. These features are specific to the polymers and should be taken into account in the development of theories and models of glass formation.

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