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## Why many polymers are so fragile

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**Abstract**
Many polymers exhibit extremely high fragility and deviate from most of
the trends known for non-polymeric glass-forming systems. The analysis of
literature data presented here demonstrates that chain rigidity might be the main
reason for this peculiar behaviour. Based on this analysis a simple scenario is
proposed: (i) oligomers (short polymeric chains) follow trends characteristic for
non-polymeric systems; (ii) increase in molecular weight (MW) does not affect
structural relaxation significantly in the case of flexible chains; (iii) however,
it slows down structural relaxation in rigid chains tremendously. As a result,
a strong increase of $T_g$ with MW is observed for rigid polymers. This rise in
$T_g$ leads to extremely high 'apparent' fragility and failure of usual correlations
between the fragility and other parameters in rigid polymers.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Understanding the glass transition, i.e. the sharp rise of structural relaxation time $\tau_\alpha$ in a
rather narrow temperature range, remains one of the most challenging problems in condensed
matter physics. To characterize the temperature dependence of $\tau_\alpha$ the concept of fragility was
introduced and promoted by Angell [1]: systems that have strongly non-Arrhenius temperature
dependence of $\tau_\alpha$ with steep variations close to $T_g$ are called fragile, and systems that show
nearly Arrhenius dependence of $\tau_\alpha$ are called strong. The fragility index $m$ is formally defined
as

$$m = \left.\frac{\partial \log \tau_\alpha}{\partial (T_g/T)}\right|_{T=T_g}. \tag{1}$$

Essentially, it characterizes the apparent activation energy of the structural relaxation at $T_g$
normalized by $T_g$.

Many ionic and van der Waals liquids are considered to be fragile and have $m$ in the range
~60–90 [2, 3]. The fragility of almost all molecular systems is limited to $m < 100$ (although
there are a few exceptions [2, 3]). Polymers, however, appear to be much more fragile, with

many of them having $m > 150$ [2, 3]. Moreover, many correlations known for small molecules are clearly violated for many polymers. For example, the jump of specific heat at $T_g$ is usually larger in more fragile systems, but the reverse is observed in polymers [2]. Strong deviation from the Adam–Gibbs relationship between the relaxation time $\tau_\alpha$ and excess entropy $S_{ex}$ has been reported for some polymers in [4].

Thus, in many aspects polymers violate the behaviour characteristic for small molecules. What is so specific about polymers that makes them different and extremely fragile in comparison to small molecular systems? What is the reason for their extremely steep temperature dependence of the structural relaxation time? These questions are the main subject of the discussion presented in this contribution.

## 2. Role of molecular weight

The main difference between polymers and other systems is the large length of the molecules. So, the nature of the polymer-specific behaviour might be related to the chain connectivity. Analysing literature data for many polymers, we realized that there is a group of polymers, such as poly(dimethyl siloxane) (PDMS), poly(methyl phenyl siloxane) (PMPS) and poly(propylene oxide) (PPO), that show no significant dependence of fragility on molecular weight (MW) [5]. Our recent detailed analysis of polyisoprene (PIP) also found no significant dependence of fragility on MW [6]. At most, it increases ∼10% (from ∼53 up to ∼60) when the MW changes from ∼1000 up to ∼20 000 [6]. At the same time, there is another group of polymers, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), that show very strong increase of fragility with MW [7, 8]. For example, the fragility of PS almost doubles between MW ∼500 and MW ∼100 000 [8].

The same polymers appear in two different groups in an analysis performed by Colmenero and co-workers [4]. The authors compared variations of $\tau_\alpha(T)$ with variations of $S_{ex}$ estimated from thermodynamic measurements. PDMS and PIP appear in the group of polymers where $\tau_\alpha(T)$ follows the traditional Adam–Gibbs relationship:

$$\tau_\alpha(T) = \tau_0 \exp\left(\frac{C}{T S_{ex}}\right), \tag{2}$$

while PS and PMMA appear in another group, in which this relationship fails and the Kauzmann temperature $T_K$ (where the extrapolated $S_{ex}$ reaches 0) is significantly below the Vogel–Fulcher–Tammann (VFT) temperature $T_0$ ($T_0$ is defined by the VFT equation $\tau = \tau_0 \exp[B/(T - T_0)]$) [4].

Recently, a correlation between fragility and ratio of bulk to shear modulus $K/G$ in the glassy state for non-polymeric systems has been reported and rationalized in [9]. Although this correlation has been challenged in [10], our response to this critique is presented in [11], and we see fundamental reasons for the correlation between $m$ and $K/G$. Figure 1 shows this correlation with addition of a few polymers. Once again, PIP appears to be among polymers that follow the trend observed for small molecular systems, while PS and PMMA deviate significantly (figure 1(a)). However, at small MW, ∼500, PS falls nicely on the same correlation [12]. The deviation appears at higher MW and increases with increase in MW (figure 1(b)). We expect similar behaviour for PMMA, polycarbonate (PC) and other high-fragility polymers.

The following picture emerges from the above analysis:

(i) short polymer chains behave similarly to small molecules; as a result,
(ii) the polymers that do not show significant variations of fragility with MW follow the behaviour traditional for small molecules at any MW, while
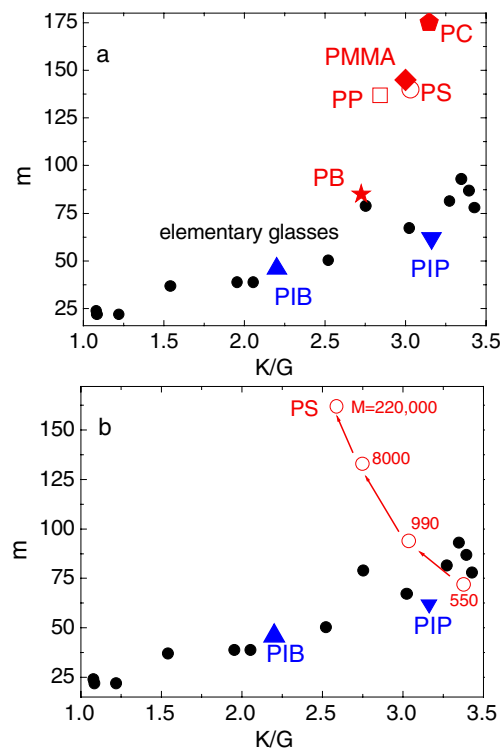
**Figure 1.** (a) Fragility versus the ratio of the bulk to shear modulus $K/G$ for elementary glasses (data from [9]) and for polymers. PIB and PIP fall on the same trend as elementary glasses while other polymers clearly deviate from this trend. (b) Data for PS with various molecular weights (shown by numbers) are added.

(iii) the polymers that exhibit strong dependence of fragility on MW deviate from this behaviour at higher MW.

## 3. Role of chain rigidity

A few recent theoretical works propose different explanations for the MW dependence of polymer fragility. Schweizer and co-workers introduced a collective dynamic barrier as the main parameter that controls the fragility [13, 14]. According to this theory, the fragility depends on the cooperativity factor $a_C$ that estimates how many 'segments' are involved in the elementary over-barrier hopping [13, 14]. $a_C \sim 1$ results in a fragility $m \sim 55$–70, while $a_C \sim 5$ brings the fragility up to $m \sim 110$–200 [14]. However, it is not clear to us how to estimate $a_C$ of the polymer and its MW dependence.

Another theoretical approach [15] suggests that the flexibility of the polymer backbone and side groups plays a crucial role in polymer fragility through frustration of chain packing. This suggestion is consistent with an earlier observation reported in [16]. PDMS and PMPS are very flexible polymers because of their Si–O–Si– backbone. PIP also has a flexible backbone due to the double-bond that decreases the energy barrier for rotation of neighbouring C–C bonds. However, PS, PMMA and PC are considered to be rigid polymers. It is obvious that an increase in the MW of flexible polymers should not significantly affect their properties,
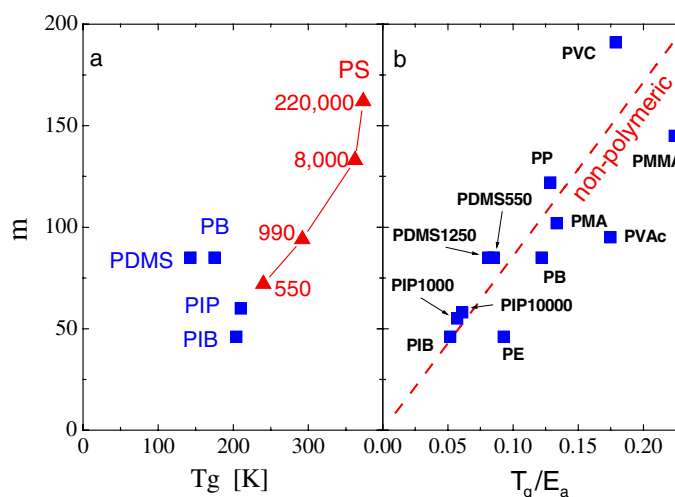
**Figure 2.** (a) Fragility versus $T_g$ for some polymers, including PS with different molecular weights. For PS, the increase in fragility correlates well with increase in $T_g$. (b) Fragility versus $T_g/E_a$. Good correlation is observed for all the polymers. The correlation agrees with the trend observed for non-polymeric systems (the latter is taken from [9]).

because motions of different parts of the molecules become decoupled on a short distance along the backbone. In contrast, rigid polymers should exhibit significant dependence of various properties, including fragility, on the MW because larger segments along the chain will be involved in structural relaxation. Thus, apparently the chain rigidity might be one of the main parameters that results in the extremely high fragility of some polymers at high MW. In some sense, this suggestion might be close to the idea of larger cooperativity parameter $a_C$ in more fragile polymers proposed by Schweizer and co-workers [14].

Qin and McKenna recently emphasized a correlation of polymer fragility and $T_g$ [17]. Usually, high-$T_g$ polymers ($T_g \sim 370$ K and higher) are extremely fragile, while low-$T_g$ polymers ($T_g \sim 210$ K and lower) have rather low fragility. The correlation presented in [17], $m \propto T_g$, is not very convincing for polymers, and there are many clear examples where the proposed correlation fails. We can compare PDMS ($T_g \sim 146$ K, $m \sim 85$) and 1,4-poly(butadiene) PB ($T_g \sim 177$ K, $m \sim 85$) to poly(isobutylene) (PIB) ($T_g \sim 205$ K, $m \sim 46$) and PIP ($T_g \sim 210$ K, $m \sim 60$). The former have lower $T_g$ but higher fragility (figure 2(a)).

Based on the construction of the fragility plot, the authors of [9, 12] proposed a relationship between fragility, $T_g$ and high-temperature activation energy of the structural relaxation $E_a$: $m \propto T_g/E_a$. We emphasize that the value of $E_a$ should be estimated from high-temperature Arrhenius behaviour of glass-forming liquids. Applying this idea to the segmental relaxation in polymers and assuming that $E_a$ does not exhibit strong dependence on MW, we arrive at the prediction that $m(\mathrm{MW}) \propto T_g(\mathrm{MW})$. This prediction is consistent with the idea of Qin and McKenna and with the correlation between the MW dependences of fragility and $T_g$ reported in [7, 18]. The data for the only polymer studied in detail, PS, support the proposed relationship (figure 2(a)). Moreover, this idea might explain why PDMS and PB with lower $T_g$ have higher fragility. The extremely flexible backbone in this polymer should result in very low $E_a$; as a result, the ratio $T_g/E_a$ might be higher than in PIB and PIP. PIP and PB have a similar backbone, but the addition of a methyl group should lead to higher activation energy in the case of PIP.

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**Table 1.**  $T_g$, high-temperature activation energy $E_a$ of segmental relaxation and fragility $m$ of polymers.

|                  | $T_g$ (K)   | $m$        | $E_a$ (kJ mol$^{-1}$) | $T_g/E_a$ |
|------------------|-------------|------------|-----------------------|-----------|
| PIB              | 205 [21]    | 46 [26]    | 33 [21]               | 0.052     |
| PE               | 231 [21]    | 46 [27]    | 20.7 [21]             | 0.093     |
| PIP (1000) [6]   | 199         | 55         | 28                    | 0.057     |
| PIP (10000) [6]  | 212         | 58         | 28                    | 0.061     |
| PDMS (550) [19]  | 138         | 85         | 13.5                  | 0.085     |
| PDMS (1250) [19] | 143         | 85         | 14.7                  | 0.081     |
| PB [20]          | 177         | 85         | 12.1                  | 0.12      |
| PVAc             | 304 [21]    | 95 [26]    | 14.5 [21]             | 0.17      |
| PMA              | 276 [21]    | 102 [26]   | 17.2 [21]             | 0.13      |
| PP               | 253 [21]    | 122 [26]   | 16.4 [28]             | 0.13      |
| PMMA             | 373 [21]    | 145 [26]   | 13.9 [21]             | 0.22      |
| PVC              | 356 [21]    | 191 [26]   | 16.6 [21]             | 0.18      |

We were able to find literature values for $E_a$ of segmental relaxation in a few polymers (table 1). We want to emphasize that the experimental values of $E_a$ should be taken at high temperatures (preferably, at $T > 2.5T_g$) where asymptotic Arrhenius behaviour is approached. We use dielectric data for PIP [6], light-scattering data for PDMS [19] and NMR data for PB [20]. The rest of the data are taken from [21] and references therein. Indeed, $E_a$ in PDMS appear to be very low ($\sim$15 kJ mol$^{-1}$), while it is much higher in PIB ($E_a \sim 33$ kJ mol$^{-1}$) and in PIP ($E_a \sim 28$ kJ mol$^{-1}$). The collected data show that the relationship $m \propto T_g/E_a$, indeed also holds for polymers (figure 2(b)). There is still a significant scattering of the points (e.g. PVAc and PVC) that might be related to estimates of $E_a$ at not high enough $T$ and/or to degradation of polymers at high $T$.

Thus the chain rigidity enters the fragility through two parameters, $E_a$ and $T_g$. It is not clear, however, which parameter can be used for characterization of the chain rigidity/flexibility. The traditional parameter is the characteristic ratio $C_\infty$ (or persistence length for semiflexible chains). However, it characterizes the size of the polymer coil but not its flexibility. For example, PDMS and PIB have the same $C_\infty \sim 6.5$, but obviously different chain flexibility. Moreover, Mattice *et al* [22] have shown that these two polymers, despite their $C_\infty$ similarity, approach the high-MW limit for the radius of gyration with different rate: it is twice as fast in PDMS as in PIB. This, together with the deficiency of the traditional definition of Kuhn segment, has been discussed in [23, 24]. The authors proposed to introduce another parameter that characterizes the dynamic bead size in polymers, $m_R$. Unfortunately, this parameter is known for only two systems: PDMS and PS. It differs in these polymers by almost ten times, while $C_\infty$ differs by only $\sim$50% [23]. Thus it remains unclear which parameter can best present the flexibility of a polymer chain, and this question is out of scope of the current paper.

## 4. A simple scenario

Based on the discussion and literature analysis presented above, we propose the following scenario. All polymers at low MW (the so-called oligomers) behave similar to small molecular systems and the relationship between temperature variations of $\tau_\alpha(T)$ and other parameters (e.g. jump in specific heat at $T_g$, change in $S_{ex}$, ratio $K/G$) should hold. Increase in MW, however, results in additional restriction of segmental mobility (increase in $\tau_\alpha$). Consequently, $T_g$ increases with MW, a fact known for all polymers with non-functionalized ends. The
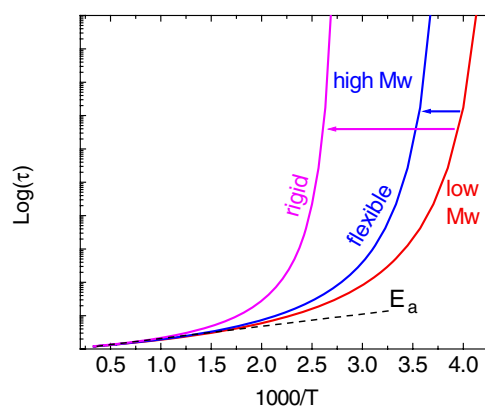
**Figure 3.** Schematic presentation of the influence of molecular weight on the temperature dependence of segmental relaxation in flexible and rigid chains.
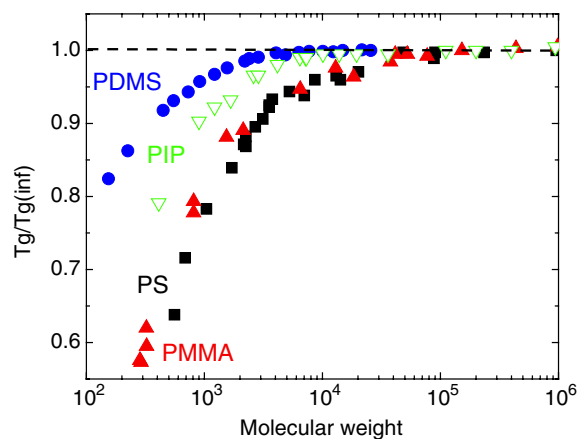


**Figure 4.** The molecular weight dependence of $T_g$ scaled by $T_g$ at high MW ($T_{g(inf)}$) for PS ($T_{g(inf)} = 373$ K), PMMA ($T_{g(inf)} = 385$ K), PIP ($T_{g(inf)} = 206$ K) and PDMS ($T_{g(inf)} = 146$ K).

increase in $T_g$ with MW for flexible chains should be weak, while much stronger restriction on segmental relaxation will be imposed in rigid polymers, and stronger dependence of $T_g$ on MW is expected in this case.

Short and long chains are expected to behave similarly at the high-temperature limit, even for rigid polymers. Figure 3 presents this scenario schematically. (i) The polymeric behaviour is rather MW independent at high $T$; (ii) restriction of segmental mobility with increase in MW results in increase of $T_g$ and steeper temperature variations of $\tau_\alpha$ (higher 'apparent' fragility). This effect is weak in flexible polymers. As a result they do not show significant dependence of fragility on MW and do not deviate much from the correlations known for small molecules. This effect might be very strong in rigid polymers. As a result, they exhibit a strong increase in steepness of $\tau_\alpha(T)$ (figure 3), i.e. in fragility, and they deviate from the behaviour characteristic for small molecules.

To support this scenario, we compare the MW dependence of $T_g$ in the same polymers, PDMS, PIP, PS and PMMA (figure 4). It is obvious that the most flexible polymer, PDMS,
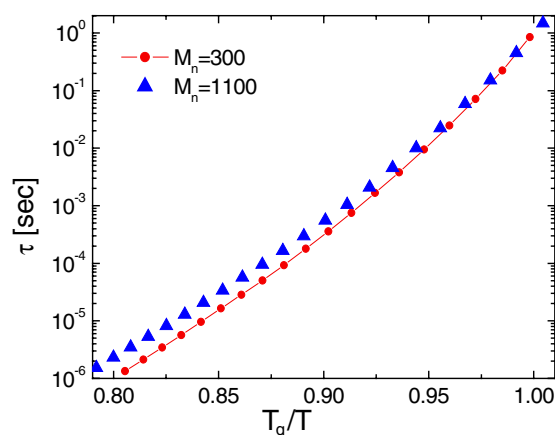
**Figure 5.** Temperature dependence of the segmental relaxation in two samples of PIB measured by dielectric relaxation spectroscopy. A decrease of fragility with increase in MW is observed.

shows the weakest variation of $T_g$ with MW, PIP being less flexible shows stronger variations, and the rigid polymers, PS and PMMA exhibit very strong MW dependence of $T_g$. A possible connection of the MW dependence of $T_g$ and chain flexibility was proposed earlier in [18, 23]. The proposed scenario is also supported by the recent detailed studies of PB [25]: they reveal a weak increase (∼20%) of fragility with MW, consistent with the weak change of $T_g$ in this polymer.

So, according to the proposed scenario, the rigidity of the chain dictates how strongly segmental relaxation will be affected by the length of a polymer chain. In another words, it controls the MW dependence of $\tau_\alpha(T)$ and $T_g$ (figure 3). A strong shift of the glass transition temperature results in a strong increase in 'apparent' fragility (figure 3), while most of the other parameters might remain the same as in a short chain. For example, the ratio $K/G$ in PS changes only by ∼20%, while $T_g$ and the fragility increase almost twice with increase in MW [12]. As a result, the correlation between $m$ and $K/G$ fails. The change of $\tau_\alpha(T)$ with MW presented schematically in figure 3 results in a strong increase of VFT $T_0$ while the Kauzmann temperature may be affected much more weakly. This explains the results presented in [4]: in rigid polymers the behaviour of $\tau_\alpha(T)$ does not follow the thermal variations of $S_{ex}$, and $T_K$ is significantly lower than $T_0$. The difference in specific heat between liquid and solid states usually decreases with temperature increase. Thus an increase in $T_g$ leads to a decrease in the specific heat jump at $T_g$. This explains the failure of the correlations between the jump in $c_p$ and fragility for polymers.

Thus, the proposed scenario provides a qualitative explanation for the specific behaviour of many polymers. According to this scenario, all polymers should show an increase of fragility with MW that should be similar to the variation of $T_g$. PIB seems to be an exception from this scenario. There are a few indirect indications that the fragility in PIB will decrease with MW [7], although its $T_g$ increases. We plan to discuss this polymer in detail in a separate paper. Here we present preliminary dielectric relaxation data for PIB (measured using a Novocontrol Concept-80 system) with two molecular weights (figure 5). The decrease of fragility with MW is obvious. We do not have any clear explanation for the specific behaviour observed in PIB. We do not exclude that the monomer symmetry and disorder in tacticity might also play a role in polymer fragility [7, 18]. In that respect, PIB presents a polymer with a symmetric structural unit and no tacticity. This requires further study.

## 5. Conclusions

The analysis presented here demonstrates that high-fragility polymers usually have high $T_g$ and a rigid backbone, results that are consistent with recent theoretical predictions [15]. Oligomers (short polymer chains) usually exhibit behaviour similar to small molecules and have intermediate fragility. Flexible chains do not show significant variations of structural relaxation with molecular weight, and their relaxation properties are similar to those observed in oligomers. High chain rigidity, however, leads to a strong dependence of $T_g$ on molecular weight and the appearance of an 'apparent' high fragility. These polymers exhibit deviations from the behaviour characteristic for small molecules. Thus, polymer-specific behaviour appears strongly only in polymers with rigid chains where the connectivity of structural units affects the segmental dynamics up to high molecular weight.

## Acknowledgments

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