

# Role of Chemical Structure in Fragility of Polymers: A Qualitative Picture

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**ABSTRACT:** Understanding microscopic parameters that control steepness of the temperature variations of segmental relaxation (fragility) and the glass transition phenomenon remains a challenge. We present dielectric and mechanical relaxation studies of segmental dynamics in various polymers with different side groups and backbone structures. The results have been analyzed in terms of flexibility of backbone and side groups of polymeric molecules, as suggested by the recent theoretical works by Dudowicz et al. A comparison of structures with identical backbones and varying side groups and identical side groups but different backbones reveals that the flexibility of side groups relative to the flexibility of the backbone is the most important factor controlling fragility in polymers, while the glass transition temperature  $T_g$  depends primarily on the backbone flexibility and the side group bulkiness (occupied volume). Based on these results and analysis of literature data we formulated a modified approach to understand the role of chemical structure in segmental dynamics: (i) Polymers with stiff backbones always have high  $T_g$  and fragility, while (ii) polymers with flexible backbones and no side groups are the strongest; (iii) however, for the most common type of polymeric structure, C–C or Si–O backbone with side groups, fragility increases with increasing “relative” stiffness of side groups versus the backbone. In this class of polymers, lowest fragility is expected when the side groups are of similar chemical structure (or flexibility) as the backbone, as in the case of polyisobutylene, one of the strongest polymers known.

## I. Introduction

Glass transition in polymeric liquids is a very important, but poorly understood, phenomenon. It is observed as a transition from the rubbery state to a glassy state upon cooling, accompanied by drastic changes in physical properties of the material in a very narrow temperature range. In particular, structural (segmental) relaxation slows down by many orders upon approaching the glass transition temperature,  $T_g$ . To quantify the steepness of the temperature dependence of the segmental relaxation time,  $\tau_\alpha$ , close to  $T_g$ , a fragility parameter,  $m$ , has been introduced:<sup>1,2</sup>

$$m = \frac{\partial \log \tau_\alpha}{\partial (T_g/T)}_{T=T_g} \quad (1)$$

It characterizes the deviation of the temperature dependence of  $\tau_\alpha$  from Arrhenius behavior. The systems that have highly non-Arrhenius temperature dependence of  $\tau_\alpha$  with steep variations close to  $T_g$  are called “fragile”, and the systems that show nearly Arrhenius dependence of  $\tau_\alpha$  are called “strong”. In other words, a fragile material shows a very abrupt change in physical properties as it approaches  $T_g$ , whereas strong materials show a strong resistance to change in properties with temperature, undergoing a relatively smooth transition from the rubbery state to the glassy state. Hence, fragility of a liquid was proposed to be a measure of structural stability,<sup>3</sup> and thus an important parameter to characterize glass formation. Fragility in polymers

has been related and/or correlated to the nonexponentiality (breadth) of segmental relaxation function,<sup>4–6</sup> rates of physical aging<sup>7,8</sup> and peculiarity of the fast dynamics.<sup>9,10</sup> It has been realized that behavior of structural (segmental) relaxation in many polymers deviates from regularities known for structural ( $\alpha$ -) relaxation in small molecular liquids.<sup>4,11–13</sup> There seems to be a “polymer specific” contribution to fragility of polymeric systems.<sup>13</sup> Understanding the structural parameters of polymers that control their fragility and differentiate them from other glass-forming systems remains a challenge.

It has been noticed earlier that polymers with rather simple, less sterically hindered structures are usually strong, while polymers with rigid or sterically hindered backbones are usually fragile.<sup>14,15</sup> In particular, the authors of ref 14 related fragility of polymers to chain stiffness and side group bulkiness. For example, polymers with rigid backbones such as polycarbonates (PC,  $m \sim 132$ ) and polyethyleneterephthalate (PET,  $m \sim 156$ ),<sup>16</sup> and polymers with flexible backbones but bulky side groups, such as polystyrene (PS,  $m \sim 118–142$ )<sup>4,16,17</sup> and polymethylmethacrylate (PMMA,  $m \sim 103–145$ )<sup>13,16,18</sup> exhibit high fragility. An examination of literature reveals that oligomers usually exhibit low or intermediate fragility ( $m \sim 60–90$ ), similar to that of small molecular weight liquids with van der Waals interactions.<sup>13</sup> Usually an increase in chain length leads to an increase in fragility in most polymers.<sup>19,20</sup> However, polymers with flexible backbones such as polydimethylsiloxane (PDMS,  $m \sim 79–100$ ) and polyisoprene (PIP,  $m \sim 55–76$ )<sup>13,16,17</sup> show no or very weak change in fragility with increase in chain length. A few ideas have been proposed to explain the fragility in polymers, based on the free volume models,<sup>20–22</sup> coupling model,<sup>23–26</sup> the generalized entropy theory<sup>27–29</sup> and cooperativity parameter that is related to the chain rigidity.<sup>30,31</sup> Each approach works well for explaining the results on certain classes of polymers, but fails for other examples. According to the recent theoretical approach predic-

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Table 1. Sample Specifications and Results

polymer	$M_n$ ( $M_w/M_n$ ) (g/mol)	source	method	repeat units	$T_g$ (K)	fragility
poly( <i>t</i> -butylstyrene) (PTBS)	1,350 (1.08)	Polymer Source Inc.	DMA	8	318	71 ± 6
	132,000 (1.04)	Polymer Source Inc.	DMA	825	407	141 ± 20
poly(4-methylstyrene) (P4MS)	900 (1.22)	Polymer Source Inc.	DMA	8	299	75 ± 4
	40,000 (1.06)	Polymer Source Inc.	DMA	355	381	121 ± 7
poly( $\alpha$ -methylstyrene) (PaMS)	700 (1.16)	Polymer Source Inc.	DMA	6	303	74 ± 3
	160,000 (1.04)	Polymer Source Inc.	DMA	1,356	406	149 ± 15
poly(cyclohexylmethacrylate) (PCHMA)	3,000 (1.15)	Polymer Source Inc.	DS	16	336	71 ± 6
	19,000(1.07)	Polymer Source Inc.	DS	112	371	80 ± 5
	165,000 (1.74)	Scientific Polymer	DS	403	377	83 ± 5
poly(phenylmethacrylate) (PPhMA)	82,000 (1.84)	Scientific Polymer	DMA	982	389	92 ± 10
poly(benzylmethacrylate) (PBM)	71,000 (2.21)	Scientific Polymer	DS	473	320	89 ± 4
poly(diphenoxyphosphazene) (PDPZ)	1,145,000 (1.51)	Scientific Polymer	DS	3,534	252	104 ± 6
poly(cyclohexylethylene) (PCHE)	50,000 (1.03)		DMA	455	394	82 ± 6
	135,000 (2.09)		DMA	2,573	406	117 ± 6

tions, chain connectivity imposes restrictions on movement of individual repeat units, leading to inefficient packing and higher fragility.<sup>27,29</sup> As a result, an increase in chain length frustrates the packing ability of rigid polymers more than it does in flexible polymers and in that way exerts a stronger influence on their fragility. This approach emphasizes the importance of flexibility/rigidity of both backbone and side groups.<sup>27</sup> However, even this approach fails when one compares PDMS with polyisobutylene (PIB): both have the same symmetric side groups and PDMS has much more flexible backbone, but significantly higher fragility, in contrast to the theoretical expectation.

In this work we attempt to make further advances in understanding the role of chemical structure in polymeric fragility. We present new systematic studies of the role of side groups, their bulkiness and flexibility, and of the role of the backbone flexibility in temperature dependence of segmental relaxation. Based on these results and analysis of literature data, we suggest a modified approach that connects fragility of polymers to peculiarities of their chemical structure.

## II. Experimental Results

**II.1. Materials.** The list of studied polymers with their molecular weights, polydispersity and experimental method used to study segmental dynamics are presented in Table 1. The chemical structures of the polymers are shown in Figure 1. All samples were acquired from commercial sources (listed in Table 1), except poly(cyclohexylethylene) (PCHE), which was synthesized by us using the catalytic hydrogenation of polystyrene.<sup>32</sup> We have measured  $M_n$  and  $M_w/M_n$  values for samples received from Scientific Polymer using GPC (Wyatt Dawn EOS multiangle laser light scattering detector with Waters model 410 differential refractometer concentration detector). The values for other polymers are taken from their respective sources.

We chose the first group of polymers that resembles polystyrene (PS) chemical structure: poly(4-methylstyrene) (P4MS), poly( $\alpha$ -methylstyrene) (PaMS), and poly(*t*-butylstyrene) (PTBS). Their analysis shows the effect of additional alkyl groups of different sizes, and structures on the phenyl ring of the styrene repeat unit. Comparison of PCHE and PS shows the effect of a flexible cyclohexyl ring versus the flat, aromatic ring. The effect of aromaticity on  $T_g$  and fragility has also been demonstrated by comparing poly(phenylmethacrylate) (PPhMA) and poly(cyclohexyl methacrylate) (PCHMA). Poly(diphenoxyphosphazene) (PDPZ) has a unique structure, with a more flexible, inorganic N=P backbone, and bulky but symmetric diphenoxy side groups. We specifically exclude any highly polar polymers from the studies presented here to avoid influence of strong intermolecular forces, which can complicate the interpretation of chemical structure effects on fragility.

**II.2. Dielectric Spectroscopy (DS) Measurements.** The complex dielectric permittivity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$  was measured in the frequency range 1 mHz to 10 MHz using Novocontrol Concept 80 broadband dielectric spectrometer equipped with Alpha Imped-

ance Analyzer. These dielectric spectroscopy measurements were performed by placing the sample between the electrodes of a parallel-plate capacitor made of brass. Sample capacitor was mounted in measuring header and placed inside cryostat. Temperature was changed using a Novocontrol Quattro temperature control unit that provides temperature stability of 0.1K by nitrogen gas flow.

**II.3. Dynamic Mechanical Analysis (DMA).** Some of the samples have very weak dipole moments, below the limit detectable by the dielectric spectrometer. Others have high values of dc-conductivity, which makes it impossible to discern the dielectric loss spectrum with sufficient accuracy. Such samples were studied using dynamic mechanical analysis, because of its insensitivity to electrical and dielectric properties of samples. This technique, however, does not offer the advantage of broad frequency range covered by the dielectric spectroscopy. Oscillatory shear measurements were made using a Rheometrics RDA-II. Isothermal testing was performed at temperatures within the  $\alpha$ -relaxation viscoelastic region using a frequency range from 0.001 to 100 rad/s and strain amplitude of 0.2%. A parallel plate sample geometry was used with a diameter of 8 mm and a gap of 3 mm.

**II.4. Determination of Fragility.** The dielectric and mechanical loss spectra were fit to a Havriliak–Negami distribution function. The characteristic relaxation time was obtained as the reciprocal of the frequency of the maximum of the HN fit function,  $\tau = (2\pi\nu_{\max})^{-1}$ .  $T_g$  was calculated at  $\tau_\alpha = 100$  s, using the Vogel–Fulcher–Tamman (VFT) equation:

$$\tau = \tau_0 \exp[B/(T - T_0)] \quad (2)$$

where  $\tau_0$ ,  $B$  and  $T_0$  are VFT fit parameters and  $T$  is temperature. Some illustrative examples of the fragility plot are shown in Figure 2. Fragility was calculated using the equation

$$m = \frac{BT_g}{(T_g - T_0)^2 (\ln 10)} \quad (3)$$

that is obtained by substituting eq 2 into eq 1. Since this estimate of fragility uses all the measured data via the VFT fit, it is more accurate than a simple measure of the slope at  $T_g$  evaluated directly from a few experimental data points in close proximity to  $T = T_g$ . The error bars for fragilities estimated from mechanical relaxation are larger compared to dielectric data. The smaller number of experimental points and narrower range of accessible  $\tau$  in mechanical measurements leads to larger error-bars in the VFT fit parameters. This results in large errors in estimated values of fragility. The calculated values of  $T_g$  and fragility are reported in the Table 1.

**II.5. Dependence of  $T_g$  and Fragility on Chemical Structure and Molecular Weight.** Figure 3a shows  $T_g$  of substituted polystyrenes as a function of chain length (number of repeat units,  $N$ ). A comparison between polystyrene and polymers with alkyl substituents on the phenyl ring (PTBS, PaMS, P4MS) shows that all the substituted polymers exhibit higher glass

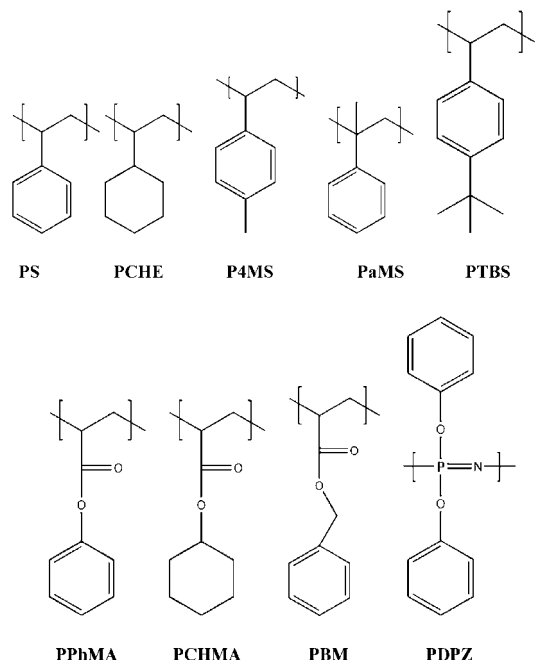


Figure 1. Chemical structures of polymers studied in this work.

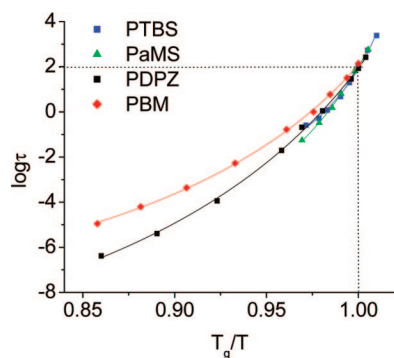


Figure 2. Relaxation time vs  $T_g/T$  (the fragility plot) for some polymers: experimental data (symbols) and their corresponding VFT fits (lines).

transition temperatures than polystyrene at comparable chain lengths. Figure 3b shows  $T_g$ s for PCHE, PCHMA, PBM and PPhMa.  $T_g$  of PBM is very low compared to PCHMA. Both, PCHE and PCHMA show a moderate change in  $T_g$  with MW. PCHMA and PPhMa have similar  $T_g$  at a comparable chain length.

Figure 4a presents the molecular weight dependence of fragility in substituted polystyrenes. Fragility increases with chain length for all these molecules. All the substituted oligomers and polymers seem to have fragility comparable to PS within the margin of error.

A comparison of fragility of polymers with cyclohexyl versus phenyl side groups is presented in the Figure 4b. PCHE has fragility lower than PS at comparable chain length. Also PCHMA is less fragile than both PPhMa and PBM. Thus substitution of the phenyl ring by the cyclohexyl ring decreases the fragility of the polymer. It appears that PCHMA is not only the least fragile among the polymers studied here, it also shows a relatively weak MW dependence of fragility. In contrast, PCHE shows the steepest increase in fragility with molecular weight that might be related to rather broad polydispersity of the sample used (Table 1).

### III. Discussion

It is known that  $T_g$  of a polymer is low if the barriers for segmental motion of the backbone are low. These barriers depend strongly on the chemical structure of the backbone and side groups. Stiff backbones and bulky side groups present

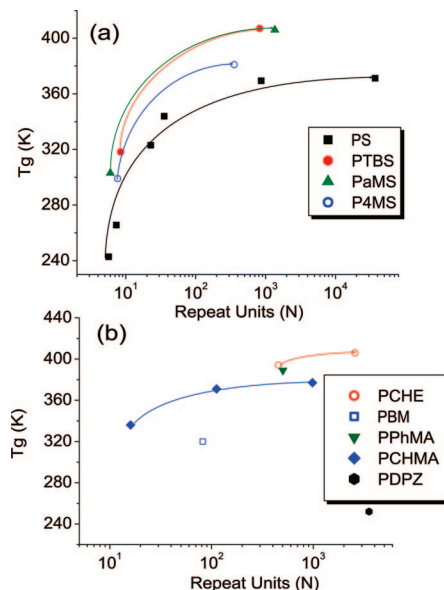


Figure 3. The molecular weight dependence of  $T_g$  in studied polymers: symbols, experimental data; lines represent expected trend and serve more as a guide. PS data are from ref 19.

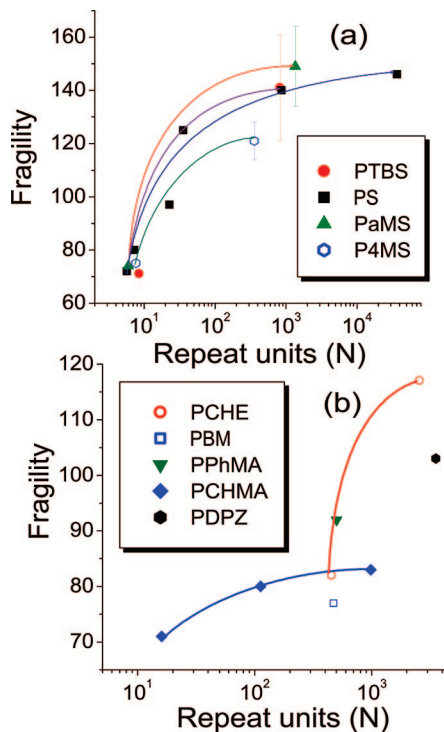
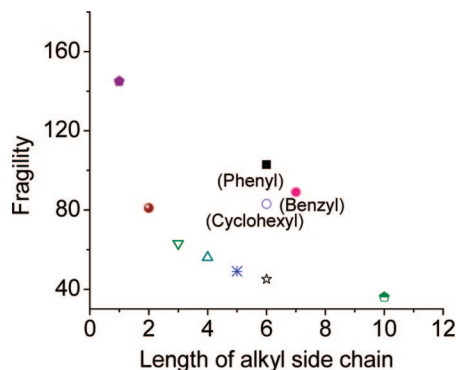


Figure 4. The molecular weight dependence of fragility: symbols are experimental data, and lines are guides for the eyes.

hindrances in the activation of the backbone segmental motion, raising the glass transition temperature. However, according to the recent theoretical work by Dudowicz et al.,<sup>27–29</sup> fragility in polymeric systems is related to their packing ability: rigid chains and bulky side groups present difficulty in packing these complex shaped molecules and leave excess free volume resulting in higher fragility. On the other hand, flexible molecules are less fragile by virtue of their better packing ability during vitrification. Below we analyze the results presented here in the framework of this approach.

**III.1. Effect of Alkyl Substituents.** The presence of various alkyl substituents on the phenyl ring makes the side groups on P4MS and PTBS more bulky compared to polystyrene. A similar





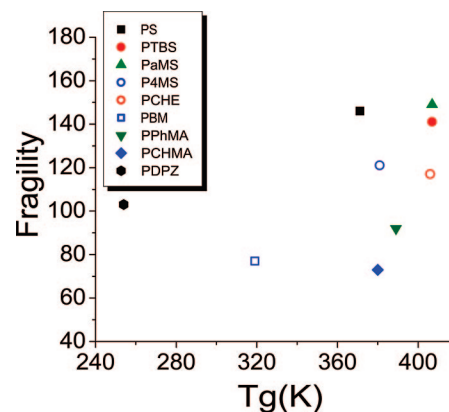
**Figure 5.** Fragility of poly(alkylmethacrylates) as a function of alkyl side chain length (part of the data are from refs 16 and 35). The unlabeled points represent the length of side chains in terms of number of methylene units attached to the methacrylate repeat unit.

effect comes into play in PaMS where the methyl group is attached to the backbone ( $\alpha$ -carbon). These substituents increase the overall bulkiness of the repeat unit, and congest the segmental mobility, resulting in increased  $T_g$  of these polymers, as observed in Figure 3a.

However, the fragility of two of the substituted polymers (PTBS and PaMS) is comparable to fragility of PS, while that of P4MS is lower than that of PS within experimental error (Figure 4a). The reason for this insignificant change could be related to a little change in the overall flexibility of the side group by addition of extra methyls. Linear alkyls are considered flexible spacers and are expected to decrease the fragility. An effect of this type of structure is observed in case of poly(alkyl methacrylates), where fragility decreases with increasing length of the alkyl side group (Figure 5). The decreased fragility is attributed to a smaller coupling parameter in chains with longer alkyl side groups.<sup>33</sup> However, in case of polystyrene-type polymers, the influence of additional methyl groups on fragility is not significant.

**III.2. Effect of Non-Aromatic Ring.** An unusual behavior is observed when the phenyl ring in polystyrene is replaced with a nonaromatic cyclohexyl ring (PCHE). As indicated in Figure 4b, the fragility of PCHE appears to be lower than that of PS,<sup>4,16,17</sup> although it has a much higher  $T_g$  (406 K) compared to PS (373–375 K) of comparable chain length. The apparent reason for this unusually high  $T_g$  can be explained based on the nature of the cyclohexyl ring in PCHE. A cyclohexyl ring differs from the aromatic phenyl ring in size and flexibility. It is bulkier in size (van der Waals (VdW) volume = 83.15 cm<sup>3</sup>/mol<sup>34</sup>) compared to a phenyl ring (VdW volume = 77.10 cm<sup>3</sup>/mol<sup>34</sup>), and also slightly heavier. On the other hand, it is very flexible compared to phenyl ring, and can adopt a chair or a boat conformation, which enables PCHE to have larger number of configurational states compared to PS and also to pack more efficiently. That leads to fragility of PCHE being lower than the fragility of PS.

A comparison between PCHMA and PPhMA yields a similar result. PCHMA and PPhMA have identical structure except for the nonaromatic cyclohexyl ring substituting phenyl ring. Although their  $T_g$ s do not differ much, fragility of PCHMA ( $m \sim 83$ ) is much lower than fragility of PPhMA ( $m \sim 92$ ). A comparison of the bulkiness and flexibility of the ring structures points toward a similar trend as has been discussed for PCHE vs PS. It appears that the flexible cyclohexyl ring facilitates close packing of the side groups in PCHMA, resulting in lower fragility. And, although the cyclohexyl ring is bulkier compared to the phenyl ring, it is not directly attached to the backbone in PCHMA, as is the cyclohexyl ring in PCHE. Therefore, the effective change in volume of the repeat unit by substituting

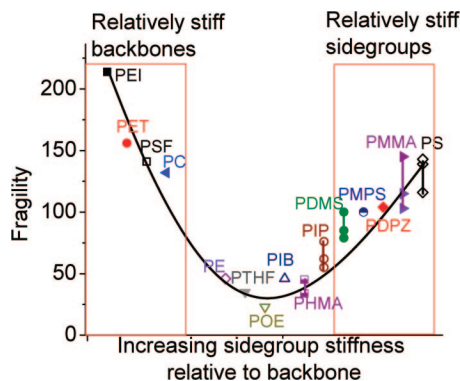


**Figure 6.** Fragility as a function of  $T_g$  for a few studied polymers.

the phenyl ring with cyclohexyl is only fractional in case of the methacrylate side group in PCHMA compared to the phenyl side group in PCHE. Hence, the observed difference in  $T_g$ s of PCHMA and PPhMA is small. Another phenyl containing methacrylate, PBM is more fragile ( $m \sim 89$ ) than PCHMA because of the stiff phenyl ring, but less fragile than PPhMA because of the extra methylene spacer connecting the phenyl ring. This results in a slight increase in side group flexibility. Also, the  $T_g$  of PBM (320 K) is significantly lower than that of PCHMA (377 K) and PPhMA (389 K) because of this extra methylene spacer in the side group. This is consistent with the results observed for poly(alkylmethacrylates) where the fragility and  $T_g$  decrease with an increase in the length of the flexible alkyl side group, as shown in Figure 5. According to Ngai et al.,<sup>33</sup> this is a result of decreased intermolecular coupling or degree of cooperativity of the  $\alpha$ -relaxation. However, all the cyclic structures (PPhMA, PBM and PCHMA) are more fragile than linear ones with the same number of carbon atoms. This happens because a ring structure is obviously less flexible than a linear structure of the same number of carbon atoms.

**III.3.  $T_g$  vs Fragility.** At the first glance, the parameters that control  $T_g$  and fragility seem to be the same. It is known that polymers with stiff backbones and bulky side groups have high  $T_g$ . Authors of ref 14 suggested that the same parameters control fragility. This idea also seems evident in the correlation pointed out by Qin and McKenna between the fragility and  $T_g$  of polymers with van der Waals interactions. According to their observations, high  $T_g$  polymers exhibit high fragilities.<sup>16</sup> This trend, however, breaks down for many systems.<sup>13</sup> Their compilation of literature data shows strong scattering of the points presenting fragility of polymers vs. their respective  $T_g$ s. The fragilities and  $T_g$ s of polymers studied in this work also show a broad scattering of the data without clear trend (Figure 6). On the low  $T_g$  side of the graph, there is PDPZ with  $T_g \sim 252$  K and a relatively high fragility ( $m \sim 104$ ). PCHMA appears on the other extreme with a rather low fragility ( $m \sim 83$ ) for a relatively high  $T_g \sim 377$  K. This analysis has a clear conclusion: the molecular parameters that affect fragility are not the same parameters that control  $T_g$ . So, what is the difference?

Dudowicz et al.<sup>27–29</sup> have proposed an approach based on a generalized entropy theory to predict the polymeric fragility as a function of molecular structural parameters: fragility reflects frustration in packing of long molecules with steric hindrances coming from stiffness of the backbone and of the side groups. They emphasize that polymers with simple backbones and side groups are the strongest glass formers (e.g., polyisobutylene and polyolefins),<sup>28</sup> while flexible chains with bulky, stiff side groups (such as polystyrene) are relatively fragile, and polymers with bulky, stiff backbones (such as polycarbonate) are the most



**Figure 7.** The proposed schematic diagram of the parameters that control fragility of polymers. Symbols present known experimental value for fragility of various polymers (values of  $m$  along with references are listed in Table 2). The x-axis presents some arbitrary parameter, and the data position along the x-axis is a qualitative ranking rather than well-justified number. The solid line is a guide to the eye indicating the proposed trend.

fragile. Thus, according to the theoretical predictions,<sup>36</sup> the rigidity/flexibility of the chain backbone and of the side groups are essential parameters governing the fragility in polymers. However, there are some known examples that seem to disagree with the above scenario. For instance, poly(dimethylsiloxane) (PDMS) has a very flexible backbone and an extremely low  $T_g \sim 145$  K, yet PDMS is significantly more fragile ( $m \sim 80$ – $100$ <sup>4,13,16</sup>) than PIB ( $m \sim 46$ <sup>16</sup>) that has higher  $T_g \sim 205$  K. A careful look at their structures sheds some light on this puzzle.

**III.4. PDMS vs PIB.** PDMS and PIB have flexible backbones and identical flexible side groups: symmetrically positioned  $\text{CH}_3$ . PDMS has a much lower  $T_g$  than PIB because the Si–O backbone is significantly more flexible (has a characteristic energy barrier for conformational changes lower than 2 kJ/mol<sup>37</sup>) than the C–C backbone in PIB (energy barrier in the range 18–25 kJ/mol<sup>37,38</sup>). However, fragility of PDMS is about twice higher than that of PIB. Thus the flexibility of the backbone does not always lead to a low fragility. It appears that the side groups in case of PIB are chemically similar to the backbone, having also similar activation energy  $\sim 14$  kJ/mol.<sup>39</sup> So, motions of both, backbone and side groups, will slow down at similar temperatures leading to very efficient packing of this molecule and the low fragility of this polymer. On the other hand, the methyl side groups in PDMS have the energy barrier  $\sim 7$  kJ/mol,<sup>39</sup> which is much higher than the activation energy for the backbone motions. This means that the methyl groups that we usually consider to be flexible units, in the case of PDMS appear as rigid side groups in comparison to the flexible backbone. This results in poor packing and stronger deviation from Arrhenius behavior of relaxation time in PDMS. Thus, the difference in *relative side group stiffness* (side group stiffness relative to the backbone stiffness) between these two polymers may be the reason behind the significant difference in their fragility.

**III.5. PMPS vs PaMS.** A comparison between another set of similar structures, poly(methylphenylsiloxane) (PMPS) and PaMS, does not yield the same result. Both of them have identical side groups (phenyl ring and methyl group) and flexible, but different, backbones (Si–O and C–C respectively). Between these two polymers, PaMS exhibits both higher  $T_g$  and fragility compared to PMPS,  $T_g \sim 406$  K vs  $T_g \sim 243$  K and  $m \sim 149$  vs  $m \sim 100$ , respectively. However, in this case, one of the side groups (phenyl) is very large and stiff compared to the other (methyl), being able to cause stronger congestion between chains, frustrate their packing and/or increase the cooperativity

**Table 2.** Literature Values of Fragility and  $T_g$  for Some Polymers

polymer	fragility	$T_g$ (K)
polyoxyethylene (POE)	23 <sup>16</sup>	232 <sup>16</sup>
polytetrahydrofuran (PTHF)	35 <sup>16</sup>	189 <sup>16</sup>
polyethylene (PE)	46 <sup>16</sup>	237, <sup>16</sup> 231 <sup>13</sup>
polyisobutylene (PIB)	46 <sup>16</sup>	201, <sup>16</sup> 205, <sup>13</sup> 200 <sup>4</sup>
polyhexylmethacrylate (PHMA)	45, <sup>16</sup> 34 <sup>16</sup>	280.5 <sup>16</sup>
polyisoprene (PIP)	55, <sup>13</sup> 62, <sup>16</sup> 76 <sup>16</sup>	199, <sup>13</sup> 200 <sup>16</sup>
polydimethylsiloxane (PDMS)	79, <sup>4</sup> 85, <sup>13</sup> 100 <sup>16</sup>	143, <sup>13</sup> 146 <sup>16</sup>
polymethylphenylsiloxane (PMPS)	100 <sup>16</sup>	243 <sup>15</sup>
polymethylmethacrylate (PMMA)	103, <sup>16</sup> 115, <sup>17</sup> 145 <sup>12</sup>	367, <sup>16</sup> 373 <sup>13</sup>
polystyrene (PS)	116, <sup>4</sup> 139, <sup>16</sup> 143 <sup>17</sup>	375, <sup>16</sup> 373 <sup>4</sup>
polycarbonate (PC)	132 <sup>16</sup>	423.5, <sup>16</sup> 418 <sup>5</sup>
polyethyleneterephthalate (PET)	156 <sup>16</sup>	342 <sup>16</sup>
polysulfone (PSF)	141 <sup>4</sup>	459 <sup>4</sup>
polyetherimide (PEI)	214 <sup>16</sup>	480.6, <sup>16</sup> 478.5 <sup>4</sup>

of molecular motions. The immobility of phenyl ring pushes the  $T_g$  of both PMPS and PaMS to be almost a factor of 2 greater than that of PDMS and PIB, respectively. However, inflexibility of the phenyl ring could not affect significantly the fragility of PMPS relative to PDMS (they already have relatively inflexible methyl group), while it leads to significant increase in fragility between PIB and PaMS. Thus once again high rigidity of the phenyl ring relative to the flexibility of the C–C backbone leads to a significant increase in fragility. This idea is further supported by the example of poly(diphenoxyphosphazene) (PDPZ), another polymer studied in this work. It has a very flexible inorganic N=P backbone, with two bulky phenoxy side groups attached to phosphorus. The  $T_g$  of PDPZ is low (252 K) by virtue of its backbone flexibility. However, the presence of very bulky substituents results in a relatively high fragility ( $m = 104$ ) due to the reasons discussed above.

### III.6. Relative Flexibility of Backbone and Side Group.

The above examples suggest that backbone flexibility is the controlling factor in determining the  $T_g$  of a material. The effect of bulky side groups appears to have a secondary influence on  $T_g$  of polymers. Polymers with flexible backbones are usually also less fragile. However, as the *side group stiffness relative to the backbone* increases, its effect may offset the influence of backbone flexibility, and become a more decisive factor in controlling the polymer fragility. On the other hand, polymers with very rigid backbones containing aromatic rings, such as polycarbonates (PC), polyethyleneterephthalates (PET) and polyimide (PI), are inherently fragile because of inefficient packing of rigid chains.

These results point toward one common picture. It is not the individual flexibility of backbone and side group units but their relative flexibility that controls the fragility parameter in most polymers. Polymers are likely to be less fragile when (i) the backbone is very flexible and there are no side groups (e.g., PTHF, PEO, PE) and/or (ii) the side groups are similar in flexibility to the backbone, (e.g., PIB). Fragility increases when either the side groups or the backbone becomes relatively stiffer than the other. This idea is illustrated in Figure 7 where fragility is plotted versus a qualitative ranking of this relative stiffness.

This representation includes values of fragility of some common polymers obtained from literature (presented in Table 2). It can be observed that polymers with relatively stiff backbones (on the left side) are the most fragile. Polymers with flexible backbones and stiff side groups (on the right side) are also relatively fragile. However, polymers with very flexible backbones (in the middle) and no side groups (PTHF, PEO, and POE) are the least fragile. PIB is found to be the least fragile among all the polymers with side groups. PIB has a unique structure where the methyl side groups are chemically similar to the backbone, and have similar energy barriers for rotation,

allowing very efficient packing. However, fragility increases with increasing difference between side group and backbone stiffness.

We have attempted to present a simple picture by breaking down the effect of various structural parameters on dynamics of glass transition. It works best for simple polymer structures containing a simple backbone and side groups. Furthermore, based on the understanding of the effect of chemical structure, it is possible to summarize the expected fragility of different classes of polymers with only van der Waals interactions.

1. Polymers with very stiff backbones, such as PC, PET and PEI, are expected to be the most fragile. Fragility and  $T_g$  are both expected to increase with increasing backbone stiffness.

2. Polymers with very flexible backbones, and no side groups, such as POE, PE and PTHF, are the least fragile. The fragility decreases with increasing backbone flexibility, e.g., by addition of ether linkages.

3. Addition of bulky and inflexible side groups causes the polymers with flexible backbones to become relatively fragile and also increases  $T_g$ . The fragility increases with increasing relative side group stiffness and bulkiness, for comparably flexible backbone. A polymer with side groups is expected to be least fragile when the side groups have stiffness similar to the backbone.

4. Symmetrically substituted polymers are likely to be less fragile than asymmetric polymers, as can be observed from comparison of PIB ( $m \sim 46$ ) and polypropylene ( $m \sim 137$ ).<sup>14</sup> The role of symmetry requires additional attention, and some ideas have been proposed.<sup>40</sup>

However, there are several questions that still remain unanswered about polymer fragility. It is not known whether fragility will decrease if stiff polymers such as PET and PC are substituted with flexible side groups, as happens in case of poly(alkyl methacrylates). Moreover, will the fragility in these polymers drop down also if side groups with stiffness similar to the backbone (i.e., rather stiff side groups) are added, as it is observed in the case of PIB? It is also not clear what drives the molecular weight dependence of fragility. According to the theoretical predictions,<sup>27,31</sup> fragility can only increase with molecular weight. This is indeed the common behavior for many polymers, also presented in this paper (Figure 4). However, we know example of PIB where fragility decreases (although not significantly) with increase in molecular weight.<sup>40,41</sup> In the case of poly(alkyl methacrylates), the fragility of polymers with long side chains is lower than the commonly observed range ( $m \sim 60$ – $90$ ) for oligomers (Figure 5). Will these polymers also exhibit decrease in fragility with molecular weight? Increasing molecular weight imposes relaxation and packing constraints via chain connectivity and simultaneously diminishes any plasticizing effects of mobile chain ends. Fragility is a  $T_g$ -scaled parameter, so understanding the relative influences of chain length on the glass transition and the temperature dependence of segmental relaxation is key to explaining increases, invariance, or even decreases in fragility with increasing molecular weight for different polymers.

It might be helpful to provide quantitative comparison of the stiffness of backbone and side groups based on activation energies of the motion of individual units. These data could be obtained from computer simulations. However, calculation of activation energies of complex polymer structures, containing several chemical groups (e.g., PC, PET), remains a challenge. More theoretical modeling in this area is desired and will help quantify the effect of the above-mentioned structural parameters on glass formation.

#### IV. Conclusions

Analysis of the presented experimental results and of the literature data has enabled us to separate the factors that control

$T_g$  and fragility in polymers with van der Waals interactions. A comparison of polystyrene with similar structures reveals that alkyl substituents on the phenyl ring in polystyrene drive the  $T_g$  higher but does not affect significantly fragility. Another effect is observed by substituting the phenyl ring with a bulkier but more flexible cyclohexyl ring: in that case  $T_g$  increases while fragility decreases significantly. These observations suggest that  $T_g$  and fragility have different dependences on chemical structure of polymers.  $T_g$  depends more on the size or bulkiness while fragility is controlled by the flexibility of the side groups in polymer structures containing simple backbones and side groups. Thus, the direct correlation between  $T_g$  and fragility breaks down. A qualitative concept has been proposed that estimates the fragility of different classes of polymer structure (Figure 7). This concept follows the idea of Dudowicz et al.,<sup>27</sup> but emphasizes stronger the relative flexibility of the side groups and the backbone. It has been noticed earlier that polymers with very stiff backbones, such as PC and PET, are the most fragile, and polymers with very flexible backbones and no side groups such as PTHF and PE are the strongest. We observe that for flexible polymers containing side groups, the fragility increases with increasing relative stiffness of side groups. However, among these polymers, the fragility is expected to be the lowest when the side group flexibility matches that of backbone, as in the case of PIB. Several questions, however, remain unanswered and require more theoretical work. New approaches to calculate the total flexibility of complex structural units, taking into account size, stiffness and symmetry may help quantify the effect of these parameters on polymer fragility.

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