6816 *Macromolecules* **2009**, *42*, 6816–6817
DOI: 10.1021/ma900666z

Macromolecules
NOTE

Molecular Weight Dependence of Fragility in Polymers

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Received March 27, 2009; Revised Manuscript Received July 14, 2009

In a recent contribution we reinvestigated the molecular weight (M in g/mol) dependence of the glass transition temperature T_g for a series of polystyrenes (PS), polydimethylsiloxanes (PDMS), and polybutadienes (PB), as determined from dielectric spectroscopy.[1] A broad range of M was studied including the low M limit. The data have been found to be compatible with assuming a discontinuous change of $T_g(M)$, with two kinks at M_1 and M_2. Tentatively, we have argued that M_1 signals the crossover from simple liquid to Rouse dynamics, and M_2 signals the onset of entanglement dynamics. Yet, the statement has been afterward challenged.[2] Discontinuous behavior has also been found when analyzing fragility $m(M)$ as well as $T_0(M)$ from the Vogel−Fulcher−Tammann (VFT) equation (cf. eq 1). In agreement with other reports,[3,4] $m(M)$ follows $T_g(M)$ for polymers.

Here we will show that, although T_g as well as m may change significantly with M, the ratio $m/T_g = F$ is constant above M_1 for a series of the same polymer. Thus, fragility m appears not to be an appropriate quantity to be discussed for polymers at least. Given this, we will demonstrate that above M_1 the segmental correlation time can be expressed by an M independent function $\tau_\alpha = f(T-T_g)$. We mention that this scaling has been tested before and may be motivated within free volume ideas.[3,5,6]

The quantity F is the magnitude of the slope of lg $\tau_\alpha(T)$ at T_g, that is, $F = -\mathrm{d}\lg\tau_\alpha/\mathrm{d}T|_{T=T_g}$ (cf. eq 1). In Figure 1 we display the results for $F(M)$, including now also data for polyisoprene (PI). The quantity F turns out to be M independent above a certain M though different for the various polymers. This is quite remarkable because, for example, in the case of PS, T_g changes by about 111K in the range where F is constant. At low M deviations from F = const are discernible most prominently for PS for which F strongly increases with further decreasing M. This may indicate the crossover to an elementary liquid, that is, a nonpolymeric system.

The fact that for a given polymer F is constant for different M indicates that the derivative of lg τ_α with temperature at T_g is independent of the actual value of $T_g(M)$, and the natural variable of τ_α is rather T than $1/T$. Direct comparison of τ_α is possible when plotting the data as a function of $T - T_g$. Examples are presented in Figure 2. Master curves are recognized for $M > M_1$. Inspecting the low M limit, deviations from the master curve are obvious in particular for PS in accordance with the deviations of $F(M)$ at low M in Figure 1.

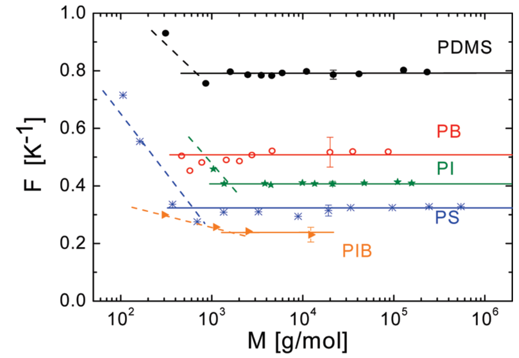

Figure 1. Quantity F as a function of molecular weight M for polystyrene (PS), polydimethylsiloxane (PDMS), polyisoprene (PI), polybutadiene (PB), and, for comparison, polyisobutylene (PIB).[8] Straight lines: guide to the eye.

We interpolated $\tau_\alpha(T)$ by applying the VFT eq, explicitly

$$\lg\frac{\tau_\alpha}{\tau_0} = \frac{D}{T - T_0} \qquad (1)$$

where the parameter D is found to be constant for all M (cf. Figure 2).[1] In these terms, fragility $m(M)$ and $F(M)$ can be expressed as

$$m = \left.\frac{\mathrm{d}\lg\tau_\alpha}{\mathrm{d}(T_g/T)}\right|_{T_g} = T_g\frac{D}{(T_g - T_0)^2} = FT_g \qquad (2)$$

Because $F(M)$ as well as $D(M)$ are constant, it follows that $T_g - T_0$ is constant, too; indeed, this is found.[1] However, it turns out that $T_g - T_0$ is not constant at $M < M_1$, and this explains the deviations in Figure 1. The exponential prefactor τ_0 of the VFT eq. is constant for a given series of polymers, but it may also change at $M < M_1$[1] (cf., PDMS data for $M = 311$ in Figure 2b).

Our results for PS do not agree with those reported by Roland and Casalini[3] whose data could not be collapsed in the way as in Figure 2 though significant scatter was observed. The findings of Plazek and O'Rourke[5] and partly those of Lin[6] are confirmed. In a rheological study of PS, Lin found a master curve in the presentation of Figure 2 for $M \geq 10500$, whereas first significant deviations occurred at $M = 5000$, which increased with lower M. However, the deviations are opposite to the ones found by us: F appears to decrease instead to increase at low M. As demonstrated in ref 1, we also cannot confirm the statement that m is independent of M in some cases,[3,4] as we always find $m \propto T_g$ for $M > M_1$, and T_g itself is a function of M . However, when $T_g(M)$ is not changing much, as is the case, for example, for PDMS, the change of $m(M)$ may be small. We find for the relative change of T_g, $\Delta T_g/T_{g\max} \cong 0.30$ for PS, 0.19 for PB, 0.08 for PI, and 0.05 for PDMS in the range of F = const. Here, at least for PS and PB, m is expected to change with T_g beyond experimental uncertainties, and this is observed.[1]

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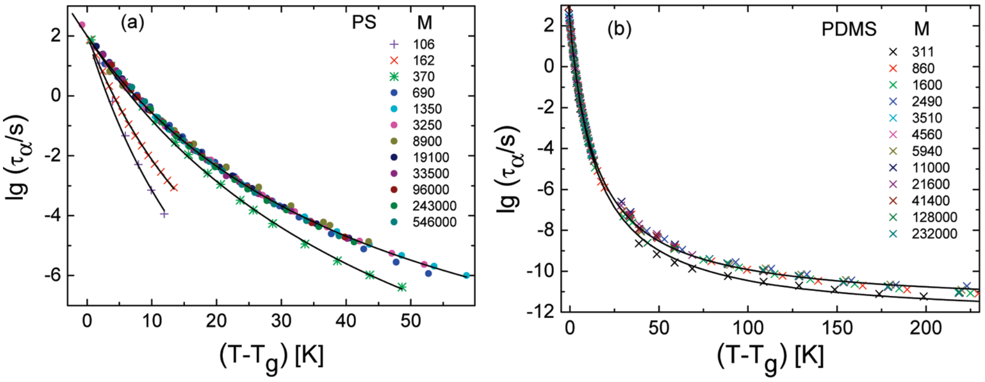

Figure 2. Correlation times obtained from dielectric spectroscopy (DS) and NMR as a function of the variable $T - T_g$: (a) polystyrene (PS), only DS data; (b) polydimethylsiloxane (PDMS), including high temperature NMR data; solid lines: interpolation by Vogel−Fulcher−Tammann law.

Recently, Sokolov and co-workers have investigated polyisobutylene (PIB),[7] and they have argued that this is an exceptional polymer as, for example, m appears to even decrease with M. We included the PIB data for F in Figure 1 (after converting them in agreement with the definition $\tau_\alpha(T_g) = 100$ s). Again, within experimental error, the data are consistent with a constant F at $M > 1000$, but for smaller M it shows a trend to increase as for the other polymers.

Concluding, the mere definition of m via the fragility plot $\tau_\alpha(T_g/T)$ introduces the M dependence of "fragility" for polymers. Therefore, fragility as conventionally defined may not be an appropriate concept to be considered, at least for polymers, but rather $F = m/T_g =$ const. characterizes a given polymer series with different m ($M > M_1$). Thus, the recently discussed[8] relationship between m and moduli or flexibility of the chain may deserve reconsideration. Some while ago we distinguished "elementary" (nonpolymer) glass formers from polymer glass formers,[9] and it appears that the crossover from a nonpolymer to a polymer liquid takes place at a distinguished molecular weight, probably M_1, which is also revealed in a discontinuous $T_g(M)$ curve.[1]

Acknowledgment. We thank A. Sokolov (Akron) for providing the relaxation data for PIB, and financial support by Deutsche Forschungsgemeinschaft (DFG) through SFB 481 and RO907/10 is appreciated. V.N.N. acknowledges support by RFBR.

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