

Test of the energy landscape interpretation of fragility in polymers

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Variation of the number of crosslinks in polyvinylethylene (PVE) networks has a marked effect on the T_g -normalized temperature dependence (“fragility”) of the segmental relaxation times, even though the local chemical environment of virtually all repeat units is unchanged. Since the heat-capacity increment at T_g is a decreasing function of the number of crosslinks, there is an inverse correlation between fragility and the heat-capacity difference between PVE’s glassy and liquid states. This result is opposite to expectations based on an energy landscape interpretation of fragility. [S0163-1829(98)00245-8]

T_g -normalized Arrhenius plots have become a common method for classifying the temperature dependence of the α process (i.e., structural relaxation in small-molecule glass formers and the local segmental motion in polymers).¹⁻³ The T_g -normalized temperature dependence, or “fragility,” has been shown to correlate with the nonexponentiality of the relaxation function,^{2,4} the chemical structure of polymers,⁵⁻⁸ the short-time diffusional properties of supercooled liquids,^{9,10} nonlinear behavior in the glassy state,¹¹⁻¹³ and even vibrational motions.¹⁴ Notwithstanding successful applications of the fragility approach, the correct interpretation of the behavior revealed by such an analysis remains an open question. The pioneering work of Angell popularized the term “fragile” to describe the non-Arrhenius character of glass formers whose structural relaxation time is a rapid function of T_g -scaled temperature near T_g . “Strong” liquids are resistant to temperature-induced changes in relaxation time or viscosity. Implicit in the use of the terms strong and fragile is the notion that the time scale for relaxation near T_g reflects the stability of the local environment (structurally not chemically) to thermal degradation.^{1,15,16}

An alternate interpretation, derived from the coupling model of relaxation, posits intermolecular cooperativity as the factor governing the temperature dependence near T_g .^{3,5,6,13} Fragile behavior implies highly cooperative local dynamics, and is expected in polymers having inflexible backbones and/or sterically hindering pendant groups. The motion of strong liquids is weakly constrained by neighboring molecules, and in the case of polymers is associated with smooth, compact, symmetrical chain backbones. Obviously, the conventional terminology “strong” and “fragile” is misleading if this viewpoint is correct; “cooperativity plot” has been suggested as an alternative designation to fragility.⁵ A number of the coupling model’s predictions regarding the relaxation properties of glass formers have been verified by experiment.^{3,5,6,13}

According to Angell,^{1,15,16} the potential energy hypersurface, governing diffusions, reorientations, and, for the case of polymers, segmental reconfigurations, has in the case of fragile liquids a plethora of minima, with low barriers between the minima. Thermal excitations readily induce energy fluctuations, causing fragile glass formers to experience a rapid breakdown of configurational structure with increase in

temperature. Hence, they exhibit strong temperature sensitivity. The specific prediction is a proportionality between fragility and the ratio of the configurational heat-capacity increment at T_g , $\Delta Cp(T_g)$, to the barrier height, a correlation observed for many small molecule glasses.^{1,15,16}

Polymers present an interesting situation. Below some high-polymer limit (ca. $M_w < 10^5$), variations in molecular weight bring about a drastic alteration of T_g and segmental relaxation times, without any change in chemical structure. Since the configurational heat capacity of polymers also becomes a function of molecular weight for low molecular weights,¹⁷ these results provide a test of Angell’s suggestion of a correlation between $\Delta Cp(T_g)$ and fragility. (For most repeat units along the chain, we at least expect no decrease in the barrier height between minima on the potential energy landscape, since the repeat unit and its chemical environment is unchanged when only the length of the polymer chain is varied.) For flexible, low- T_g polymers of varying molecular weights, the respective Arrhenius plots of segmental relaxation times are brought into coincidence by the T_g normalization scheme.^{18,19} Contrarily, for a more rigid polymer such as polystyrene, the fragility decreases (“stronger” behavior) with decreasing molecular weight.²⁰

In Fig. 1 we plot the fragility index (defined as the slope of the fragility curve evaluated at $T = T_g$) versus $\Delta Cp(T_g)$, using data reported for polydimethylsiloxane¹⁹ and polystyrene,²⁰ respectively. For the former, there is no variation of fragility with $\Delta Cp(T_g)$, a result at odds with the Angell model. For the latter, fragility is a *decreasing* function of $\Delta Cp(T_g)$, a result opposite to the model’s prediction. Thus, unlike the results for small molecule glass formers, the effect of molecular weight on the temperature dependence of segmental relaxation in polymers is not readily interpreted, in terms of a potential energy surface and the resulting heat capacity.

More recently, Angell, noting that the actual change in heat capacity at T_g is relatively small for polymers, suggested that the observed $\Delta Cp(T_g)$ may be a misleading indicator of their potential energy landscape.²¹ As molecular weight increases, the glass transition is pushed to higher temperatures, perhaps entailing higher vibrational heat capacities. A larger contribution from the vibrational heat capacity would make polymers appear “strong” by the $\Delta Cp(T_g)$ criterion, although they are, in fact, among the most fragile of glass formers.²

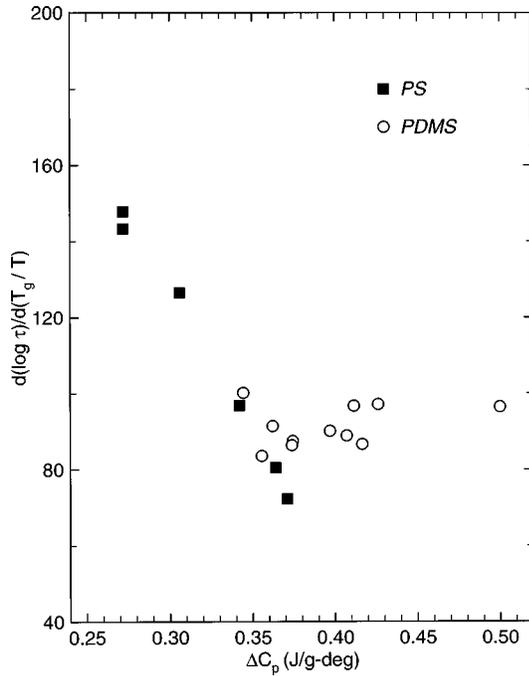


FIG. 1. The fragility for polystyrenes (■ ■ ■) and polydimethylsiloxanes (○ ○ ○) of varying molecular weights vs the heat-capacity change measured at T_g . For polystyrene, increasing molecular weight results in increased fragility yet smaller $\Delta C_p(T_g)$. Contrarily, molecular weight has no influence on the fragility of the silicone polymer. The span of the ordinate corresponds to the range of fragilities reported for polymers in general (Refs. 2 and 4).

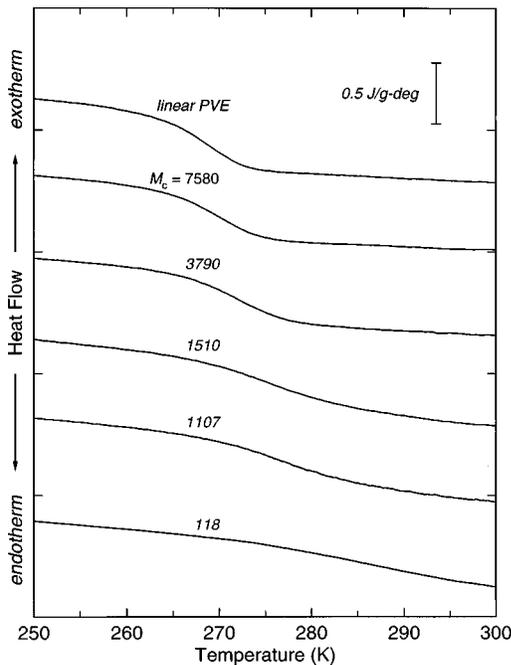


FIG. 2. Differential scanning calorimetry (cooling at 10 deg/min) for PVE networks of the indicated molecular weight between crosslinks (in units of kg/mol). There is a systematic decrease in the heat-capacity change at T_g with increasing crosslink density (smaller M_c), along with a small shift of the transition toward higher temperature.

TABLE I. Differential scanning calorimetry data for PVE networks.

M_c (kg/mol)	T_g (C)	ΔC_p (J/g deg)
(Linear polymer)	-5.0	0.456
7580	-3.7	0.434
3790	-1.2	0.423
1510	2.7	0.362
1107	3.4	0.349
118	15.4	0.276

To explore further the behavior of polymers, we compare herein heat capacities and fragilities for a series of crosslinked polyvinylethylenes (PVE). These networks were prepared from the same linear polymer, the only variation being the crosslink density (i.e., the molecular weight between crosslinks M_c). Segmental relaxation times and their dependence on temperature have been measured by dielectric spectroscopy.²² To explore Angell's ideas, we carried out differential scanning calorimetry on the networks (Fig. 2), measuring the heat capacity during cooling at 10 deg/min through the glass transition temperature. The allows assessment of the existence of any correlation between fragility and the heat-capacity change at T_g . Since all networks are comprised of the identical primary chains, the vibrational contribution to the heat capacity is essentially constant across the series. Thus, in this regard, the variation of crosslink density may have an advantage over previous studies¹⁸⁻²⁰ in which molecular weight was the variable.

As is well known,²³ crosslinks increase the glass transition temperature, although the effect is modest except at very high crosslink densities (Table I). At fixed temperature, higher T_g implies a shift of the relaxation spectrum to longer times. Relevant herein is the observation that crosslinking

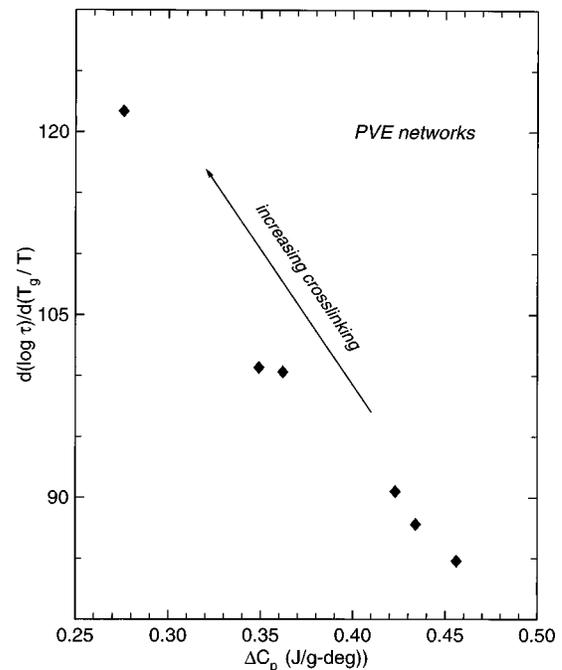


FIG. 3. The heat-capacity change at T_g , taken from the data in Fig. 2, vs the fragility index for the PVE networks.

results in significantly more fragile behavior,^{22,24} a result interpreted in terms of the degree of intermolecular cooperativity of the local segmental dynamics. Segments closer (topologically or spatially) to a crosslink junction have their motions more constrained. This is especially true for junctions of very high functionality, such as the free-radical crosslinked PVE of interest herein.²² The confluence of many network chains at the junction site imposes severe steric constraints, and consequently greater fragility.^{22,24}

The slopes of the fragility curves for segmental relaxation of the PVE networks²² are displayed in Fig. 3, as a function of the $\Delta Cp(T_g)$ measured for these same samples (Fig. 2). As the chain length between crosslinks decreases, there is a systematic reduction in the heat-capacity change at T_g . This result is well known; indeed, at sufficiently high crosslinking the glass transition is suppressed to the point of

disappearance.²⁵ More interesting is the fact that this *decrease* in $\Delta Cp(T_g)$ is accompanied by an *increase* in fragility. Such a result is diametrically opposite to the idea that the nature of the energy landscape governs the time and temperature dependences of segmental relaxation in polymers.

Polymers provide the experimentalist with the ability to vary T_g , relaxation times, and their temperature dependence, and even the shape of the relaxation function, without altering the basic chemical structure. Consequently, results on polymers provide stern challenges to theoretical models. The data presented herein reaffirm the notion that much work remains before an understanding of the behavior of glass formers can be realized.

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