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Comparison of glass formation kinetics and segmental relaxation in polymers

C.G. Robertson, P.G. Santangelo, C.M. Roland *

Chemistry Division, Code 6120, Naval Research Laboratory, Washington, DC 20375-5342, USA

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Abstract

Comparisons were made of the fragility (T_g-normalized temperature dependence of segmental relaxation times) derived from mechanical and dielectric measurements to the same quantity determined from the activation energy for enthalpy relaxation as measured by differential scanning calorimetry (DSC). For linear polystyrenes of varying molecular weight, as well as for several other polymers, there was near quantitative agreement between the two measures of fragility. However, for poly(vinylethylene) (PVE) networks, whose normalized temperature dependence by either method increased with increasing crosslink density, the relationship was not quantitative. In contrast to the assessment of fragility, the shape (breadth) of the relaxation function cannot be reliably obtained from DSC measurements. The analysis yields results which depend on thermal history, contradicting the method's assumption of thermorheological simplicity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The behavior of polymers near their glass transition is important both for fundamental understanding and for their use in various applications. Accordingly, research on the local segmental dynamics has attracted much attention, in particular the α-relaxation. The temperature dependence of properties in the vicinity of the glass transition is invariably non-Arrhenius, with the steepness of a T_g-normalized plot ('fragility curve') often used to classify relaxation behavior [1–3]. Such an approach has led to progress in revealing how chemical structure governs relaxation behavior. For example, polymers possessing flexible, nonpolar chain structures, without substantial pendant groups, exhibit narrow relaxation dispersions and weak temperature dependencies, while broad relaxation functions and segmental relaxation times which are more sensitive to temperature are generally associated with polymers whose structures engender more cooperative motion [4–8].

An interpretation of relaxation behavior in terms of thermodynamic properties has obvious appeal, for example, in providing molecular-level insights into the dynamics. The energy landscape model of Angell and co-workers [2,3,9] represents a recent attempt along these lines. While its application to small molecule glass formers has met with some success [3,10,11], results for polymers deviate from the predictions of the energy landscape model [12–16]. Recently, DiMarzio and Yang [17] developed a kinetic theory of glasses

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* Corresponding author. Tel.: +1-202 767 1719; fax: +1-202 767 0594.

E-mail address: roland@nrl.navy.mil (C.M. Roland).

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based upon equilibrium statistical mechanics. The authors suggested that their approach could provide a thermodynamic basis for the molecular weight dependence of fragility observed in some polymers. However, the DiMarzio–Yang theory remains to be exhaustively tested.

In this paper, we address the manner in which the kinetics of the glass transition, marking the departure from thermodynamic equilibrium during cooling, are related to the segmental relaxation dynamics observed by conventional spectroscopy. Our focus is on the intermolecularly cooperative α-process, although the related secondary relaxation ('β-process' [18,19]) has received increasing attention of late [20–24]. An enthalpic fragility can be defined from the effect of cooling rate on the fictive temperature, T_f. The concept of fictive temperature was introduced by Tool [25,26], to represent the temperature at which extrapolation of the liquid enthalpy equals the glassy enthalpy. Examples of determinations of T_f, which is also known as the structural temperature, can be found in the literature [27–29]. Above the glass temperature, the fictive temperature is, of course, the actual temperature. By cooling at various rates, followed by heating at a constant (arbitrary) rate through the glass transition, the variation of T_f with cooling rate can be used to define an enthalpic fragility, $m_{\Delta h}$ [29]. We adopt this method herein, to investigate the relationship, if any, of this thermodynamic quantity to the more common, dynamic fragility, m_τ, extracted from relaxation spectroscopy. The analysis is done for different series of polymers, having different variations in structure. We also note there is a related means of interpreting differential scanning calorimetry (DSC) data [30]. While it has been applied to a variety of polymeric materials, it leads to quantitatively different results, and is not pursued herein.

2. Experimental

Materials in this study included linear, atactic polystyrenes (PS, obtained from Pressure Chemical, Tosoh, and Scientific Polymer Products) with number average molecular weights (M_n) of 1.2, 2.2, 3.4, 6.1, 100, and 3700 kg/mol (corresponding to polymerization degrees of from 11 to 35 000). Polydispersities were in the range 1.04–1.10. The poly(vinylethylene) (PVE) networks [15,31] and the PS μgels [14,32] were those used in earlier studies. The molecular weights between crosslinks for the PVE were 7.6, 3.8, 1.5, 1.1, and 0.12 kg/mol (from 140 down to 2 chain units per network chain). The PS μgels, which are crosslinked nanoparticles prepared by polymerization in microemulsion [33,34], all had a total molecular weight equal to ca. 2000 kg/mol, with molecular weights between crosslinks equal to 0.94, 4.1, and 8.2 kg/mol (i.e., 9–79 repeat units per network strand).

DSC employed a Perkin–Elmer DSC 7. Typically 4 mg samples were cooled from 40 K above the glass transition, at rates, q_c, of 0.1–100 K/min. The cooling was terminated at 50° below T_g. Following a 2 min hold, samples were heated back to $T_g + 40$ K at a fixed rate of 10 K/min. Fictive temperatures were calculated from the heating data, with indium used as a calibration standard. Although in principle cooling is preferred for the determination of the glass temperature, it is difficult to calibrate given the propensity of standards to supercool. To verify that thermal lag had negligible influence on these results, a few experiments were also carried out at a 5 K/min heating rate. These yielded fragilities equal within experimental error (ca. 10%) to the results for 10 K/min. This agrees with the literature concerning the magnitude expected for thermal lag effects [35–37].

3. Results and discussion

3.1. Temperature dependence of relaxation

Representative DSC results are shown in Fig. 1 for polystyrenes of the indicated molecular weights. The abscissa for these semi-logarithmic plots is the inverse fictive temperature normalized by a reference temperature, taken to be the fictive temperature for the cooling rate, $q_c = 10$ K/min. A glass transition measured under these conditions can be considered as the temperature at which the relaxation time equals ca. 100 s [2,29,38]. Over this limited experimental time scale, the data in Fig. 1

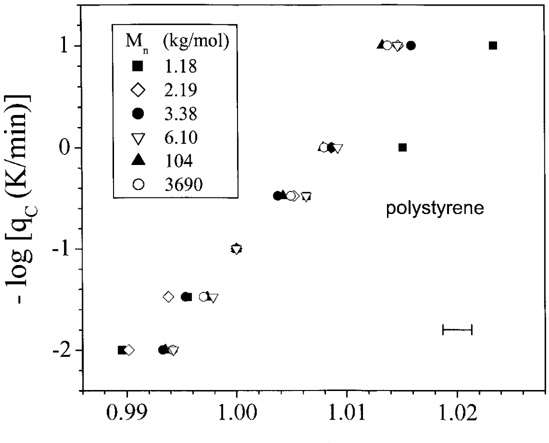

Fig. 1. Relationship between cooling rate and fictive temperature for PS, presented in the form of a fragility plot. The reference fictive temperature, $T_{f,ref}$, is the value for a cooling rate of 10 K/min.

are roughly linear. Thus, the slopes can be used to define an enthalpic fragility, $m_{\Delta h} \equiv -(\mathrm{d}\log(q_c)/(\mathrm{d}(T_{f,ref}/T_f))$. These are plotted as a function of molecular weight in Fig. 2. Also included in this figure are fragilities calculated from the DSC fictive temperatures for PS reported by Aras and Richardson [39]. There is good correspondence between the two sets of data.

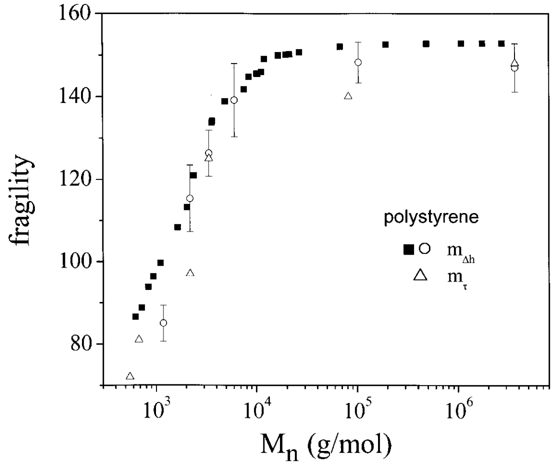

Fig. 2. Molecular weight dependence of fragility for PS, from calorimetry herein (○) and by Aras and Richardson [39] (■), and from dynamic mechanical measurements [13] (△).

More commonly, fragility refers to the T_g-normalized slope of Arrhenius plots of mechanical or dielectric relaxation times, $m_\tau \equiv \mathrm{d}\log(\tau)/\mathrm{d}(T_g/T)$. Such dynamic fragilities have been reported previously for PS from dynamic mechanical measurements [13]. As seen in Fig. 2, the enthalpic and dynamic fragilities agree both in magnitude and in their molecular weight dependence.

We can extend the comparison between calorimetry and relaxation results to other amorphous polymers, using DSC data from Hodge [40] and viscoelastic results collected by Böhmer and coworkers [41,42]. The values of DSC activation energy, Δh, of Hodge were converted to fragilities according to

$$m_{\Delta h} = \frac{\Delta h}{\ln(10) R T_g}. \tag{1}$$

In Fig. 3, we plot the two measures of fragility for polyvinylacetate (PVAc), polycarbonate (PC), polymethylmethacrylate (PMMA), and polyvinylchloride (PVC). We also include data for linear PVE and for PS from Fig. 2. These six materials span a broad range of relaxation behavior, and with the possible exception of PVC, there is good

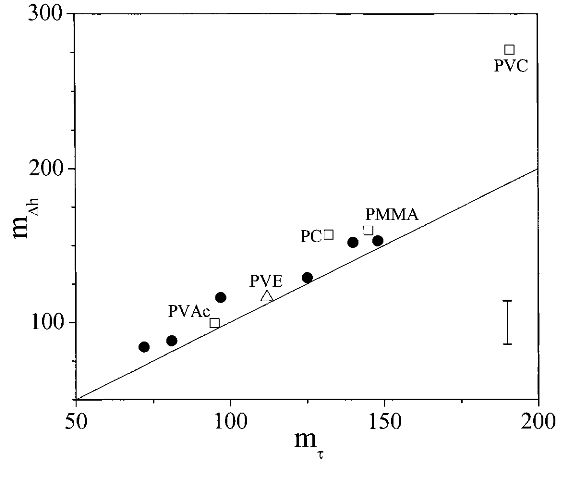

Fig. 3. Fragilities determined by DSC (using T_f at $q_c = 10$ K/min as the reference) compared to values obtained from dielectric and dynamic mechanical measurements (with T_g defined by $\tau = 100$ s) for polystyrene [13,39] (●) and other linear polymers, as indicated [40,41] (□). The error bar refers to the error associated with the DSC fragility measurements of the present study. The straight line corresponds to $m_{\Delta h} = m_\tau$.

correlation between the two measures of fragility. However, the agreement is not completely quantitative; enthalpic fragilities are larger than the values from mechanical and dielectric spectroscopy. We also note that PVC is the most dynamically fragile of any linear, amorphous polymer [41,42].

The structure of polymers can be varied by crosslinking, which alters the segmental relaxation properties [43–45]. Interpretation of their behavior is complicated by the heterogeneity inherent to networks; nevertheless, crosslinking offers a means of strongly constraining local motion with only modest changes in chemical structure. Previously, dynamic fragilities were determined for crosslinked PVE [31] and for PS μgels [14]. We carried out DSC measurements on these materials, in order to assess enthalpic fragilities. The results are displayed in Fig. 4, where it can be seen that the networks' behavior is more complex than that of the linear polymers of Fig. 3.

The crosslinked PVEs exhibit much larger enthalpic fragilities than the m_τ obtained by dielectric spectroscopy, and the discrepancy increases with the extent of crosslinking. The PVE networks are unique compared to most other polymeric networks, in that the peroxide (free radical) crosslinking leads to junctions of very high functionality [31,46]. The resulting confluence of many network chains at a junction imposes steric constraints, whose severity varies with proximity to the junction. The relaxation behavior is consequently very inhomogeneous [31].

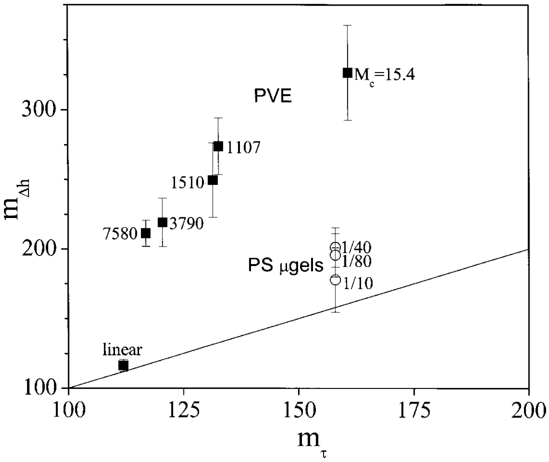

Fig. 4. Enthalpic and relaxational fragilities for crosslinked polymers: polystyrene μgels (○) from this work and Ref. [14] (having the indicated ratio of crosslinks to monomer units), and PVE networks (■) from herein and Refs. [15,31] (with molecular weight between crosslinks in g/mol as indicated). The reference temperatures are as defined if Fig. 3, and the line indicates equivalence of the two measures of fragility.

In contrast to PVE, neither the dynamic nor enthalpic fragility of the PS μgels varies significantly with the extent of crosslinking (Fig. 4). Of course, these materials are unique. Their internal structure is that of a network; however, interpenetration of molecules is negligible, and near neighbor contacts are almost exclusively intramolecular. Clearly, further research on other crosslinked systems is necessary to gain an understanding of fragility in such materials.

3.2. *Relaxation function breadth*

An attempt was made to determine the shape of the segmental relaxation function for PS, and any variation with molecular weight, from the DSC results. For mechanical and dielectric experiments, the relaxation function commonly has the Kohlrausch form [47]

$$\phi(t) = \exp[-(t/\tau)^\beta] \tag{2}$$

with the stretch exponent, β, determined by fitting Eq. (2) to isothermal relaxation data. However, to deduce β from DSC measurments, we must resort to a model for the relationship between the relaxation time and the fictive temperature. Very generally, the fictive temperature can be expressed as

$$T_\mathrm{f}(t) = T_\mathrm{i} + \Delta T(1 - \phi(t)), \tag{3}$$

where T_i is an initial temperature at which $T_\mathrm{f} = T$ (equilibrium conditions), and ΔT represents a temperature change. For continuous temperature scanning such as DSC, the Tool–Narayanaswamy–Moynihan (TNM) expression is commonly employed [38,48–51]

$$T_\mathrm{f}(T) = T_\mathrm{i} + \int_{T_\mathrm{i}}^{T} \left\{ 1 - \exp\left[- \left(\int_{t(T'')}^{t(T)} \frac{\mathrm{d}t'}{\tau(T, T_f)} \right)^{\beta} \right] \right\} \mathrm{d}T'' \tag{4}$$

which assumes a Kohlrausch function for isothermal relaxation. Details concerning the application of this expression are reviewed by Hodge [29] and Mijovic et al. [52]. The error in the obtained β is expected to be in the range of ±0.05, or about 10% [37,51].

The TNM approach requires a nonlinear function for the relaxation time, $\tau(T, T_f)$, one possibility being the relation from the Adam–Gibbs model [29,53]

$$\tau(T, T_f) = A \exp\left(\frac{D}{RT[1 - (T_2/T_f)]}\right). \tag{5}$$

In Eq. (5), D is a material constant, T_2 the Gibbs–DiMarzio transition temperature, and A is a constant. Above T_g, where structural equilibrium prevails, $T_f = T$, and Eq. (5) has the form of the Vogel–Fulcher equation [54]. Note that results very similar to Eq. (5) can be obtained using an alternative function, proposed by Narayanaswamy and co-workers [50,55].

The values of D and T_2 were determined from the enthalpic fragilities, by equating the latter to the dynamic fragility, defined according to [56]

$$m_\tau = \frac{D}{\ln(10)RT_g}\left(1 - \frac{T_2}{T_g}\right)^{-2}. \tag{6}$$

We make the assumption [57] that the relaxation time in the high temperature limit ($T \to \infty$) is less than $\tau(T_g)$ by 16 decades; that is, $\tau(T \to \infty) = 10^{-14}$ s. Letting $\tau(T_g) = 100$ s provides an initial guess for A (Eq. (5)), which is then adjusted, along with variation of the β in Eq. (4), to model the DSC heating traces. Thus, there are two adjustable parameters, β and A, with variation of the latter serving only to move the fit along the temperature scale.

Representative fits to the experimental data are shown in Fig. 5. For all molecular weights of PS, the endotherms are well described for the three decades of cooling rate used; however, the values deduced for β change with the cooling rate. As indicated in Fig. 5, there is an apparent increase in the Kohlrausch exponent with increasing q_c. This implies narrowing of the relaxation function with increasing temperature (viz. Fig. 1). Such a trend is not unusual, having previously been seen in PVE [58], polyisoprene [59], and PVAc [60]. On the other hand, a β that is nearly independent of temperature is found for many amorphous polymers, including poly(propyleneglycol) [61,62], poly(vinylmethylether) [63,64], and poly(styrene-co-vinylphenol) [16].

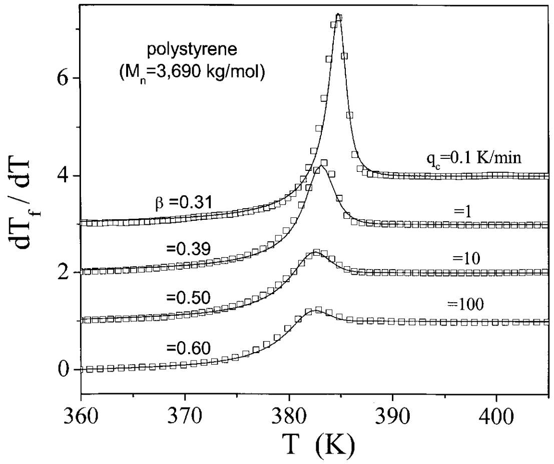

Fig. 5. Experimental DSC heating traces obtained at 10 K/min for the 3690 kg/mol polystyrene, following cooling at the indicated rates. The data are normalized such that the peak value is unity, with the curves offset vertically for clarity. The solid lines through the data are the fits obtained using Eqs. (4) and (5).

While a Kohlrausch exponent that varies with temperature is plausible, the extent of the change in β (0.3) over just a three decade variation in cooling rate is not. In addition, there is an internal inconsistency, in that Eq. (4) assumes β to be invariant to thermal history. Although attempts have been made to incorporate thermorheological complexity into the enthalpy modeling [65], for complicated thermal histories, the superposition of responses implicit in the reduced time phenomenology becomes mathematically intractable if β varies. A similar variation of the parameters obtained for PS using the TNM formalism led O'Reilly and Hodge [37] to question the validity of the approach. Other criticisms have been made of the method [29,66], including the assumption implicit in the Adams–Gibbs relation (Eq. (4)) that equilibrium relaxation times diverge to infinite values at T_2. This is contrary to both theoretical work [17] and experimental results [67] suggesting a transition from Vogel–Fulcher to Arrhenius behavior as the liquid transitions to the equilibrium glassy state.

A modification of the Adam–Gibbs model has been proposed based upon the coupling model [68,69], which allows for interaction among the 'cooperatively rearranging regions' (CRRs). This interaction modifies the observed relaxation times [68,69],

$$\tau(T, T_{\mathrm{f}}) = \left(t_{\mathrm{c}}^{\beta-1}\tau_0(T, T_{\mathrm{f}})\right)^{1/\beta}, \qquad (7)$$

where τ_0 represents the CRR relaxation time as specified by the original Adams–Gibbs model (Eq. (5)), and $t_{\mathrm{c}}(\approx 2\ \mathrm{ps})$ is a crossover time, after which interactions among the CRR become dominant. This method does not change T_2, but does give a different value for D. Using this modification of the Adam–Gibbs model, in which all parameters can be specified except β, we fit the DSC heating curves for PS. The results, however, differed negligibly from those using Eqs. (4) and (5); the problem of unrealistic variation of β with thermal history remains. We also found that the nonlinear function of Narayanaswamy [50] gave similar results.

Notwithstanding the limitations apparent in the DSC modeling, we can examine a feature of prior results on segmental relaxation in these same PS [13]. Although the fragility of PS depends strongly on molecular weight (Fig. 2), the segmental relaxation function measured by mechanical spectroscopy over this same temperature range was found to be invariant to molecular weight [13]. This is unexpected, since the breadth of the relaxation function usually correlates with fragility (smaller β associated with a larger m in Eq. (6)) [4,7,41,42,70–72]. While the β for PS enthalpy relaxation show a weak dependence on molecular weight, this dependence barely exceeds the experimental scatter. Literature values for fragility and Kohlrausch exponents are usually cited at a temperature near T_{g}. The average of the results for $q_{\mathrm{c}} = 10\ \mathrm{K/min}$ (i.e., $\tau \approx 100\ \mathrm{s}$) for all molecular weights gives $\beta = 0.46$. This value is close to the Kohlrausch exponent determined from mechanical spectroscopy [13], although the agreement may be fortuitous.

4. Conclusions

Determination of fragility from calorimetry data is a straightforward endeavor, yielding results for a variety of amorphous polymers that are consistent with, if not quantitatively equal to, values obtained by dynamic mechanical and dielectric spectroscopy. Discrepancies between the enthalpy kinetics and segmental relaxation dynamics are more apparent, however, for PVE networks of high junction functionality. Determination of the shape of the relaxation function itself from DSC measurements relies on phenomenological models of questionable validity. In particular, the thermorheological simplicity assumed by the models is contradicted by calculated results, showing Kolhrausch exponents which vary with thermal history.

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