

Departures from the correlation of time- and temperature-dependences of the α -relaxation in molecular glass-formers

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There is a well-known correlation between the shape of the relaxation function (nonexponentiality) and the temperature-dependence of the relaxation times (e.g., fragility), with broader relaxations associated with steeper T_g -normalized temperature dependences. Herein, exceptions to this correlation are described. Five molecular glass-formers, all having very similar relaxation functions, are found to exhibit a range of fragilities. We also show for two of these materials that, while pressure does not affect the breadth of the relaxation function, it substantially reduces the fragility.

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INTRODUCTION

Two important parameters characterizing the relaxation and transport properties of glass formers are nonexponentiality and fragility. The former refers to the degree to which the structural relaxation function deviates from Debye behavior, while fragility describes the rapidity of the departure of the structural relaxation time and viscosity from Arrhenius behavior, on approaching the glassy state.¹ Studies of the relationship between chemical structure and the properties of the glass transition have made clear that for a wide range of polymers and molecular glass formers, both the shape of the relaxation function and the temperature dependence of the relaxation times are related to the degree to which local structure engenders constraints on the motion from neighboring molecules.^{2,3} The correlation of these two dynamical properties with structure implies that the time- and temperature-dependences are mutually correlated. Such a correlation is indeed well-known: Steeper T_g -scaled Arrhenius plots of relaxation time are associated with broader relaxation functions.^{4,5} This correlation has become one of the more prominent features of the dynamics of super-cooled liquids and polymers (Ref. 5 has been cited over 471 times in the decade since its publication). This correlation is also an extent prediction of the coupling model of relaxation.⁶ A gross quantification of data for diverse materials leads to the relation⁵ $m = 250(\pm 30) - 320\beta$, where the fragility (or steepness index) is defined as $m \equiv d \log(\tau)/d(T_g/T)|_{T=T_g}$. τ is the structural or reorientational relaxation time, usually defined from the maximum in the dielectric or mechanical loss, and β is the stretch exponent of the Kohlraush–Williams–Watts (KWW) function.⁷ Restricting consideration to molecular glass-formers (i.e., excluding polymers, orientational glasses and alcohols) gives⁵ $m = 285(\pm 17) - 375\beta$. The sole

exception to the correlation in Ref. 5 was propylene carbonate, which has a narrow relaxation function, yet is very fragile.

The relationship between the relaxation breadth and its fragility is intended for a single process in a homogeneous material. Thus, trivial deviations from the correlation arise in blends, in which concentration fluctuations produce a distribution of local environments, and thus a distribution of overlapping peaks.⁸ Another deviation can occur in copolymers, in which the presence of chemically distinct repeat units can inhomogeneously broaden the relaxation spectrum.^{9,10} Polymer networks show a similar effect, with repeat units in close proximity to the crosslink junctions serving the role of the co-monomer.³ In this communication, we describe examples of the breakdown of the correlation between the time and temperature dependences, both at ambient and elevated pressure, which are not due to inhomogeneous broadening.

EXPERIMENT

Dielectric spectra at both ambient and elevated pressure were obtained on propylene carbonate (PC) and the isotropic phase of chiral isooctylcyanobiphenyl (8*OCB), using procedures described elsewhere.¹¹ Briefly, the sample was contained between parallel plates in a Manganin cell (Harwood Engineering), using a Novocontrol Alpha Analyzer (10^{-2} – 10^6 Hz). Pressure was applied using a hydraulic pump (Enerpac) in combination with a pressure intensifier (Harwood Engineering). Pressures were measured with a Sensotec tensometric transducer (resolution = 150 kPa). Temperature control was at least ± 0.1 K.

RESULTS

The dispersions in the respective dielectric loss spectra, corresponding to the α -process, are shown in Fig. 1, along with results from the literature for cresolphthalein-dimethylether (KDE),^{12,13} phenylphthalein-dimethylether (PDE),^{12,14} and glycerol (GLY).¹⁵ The respective tempera-

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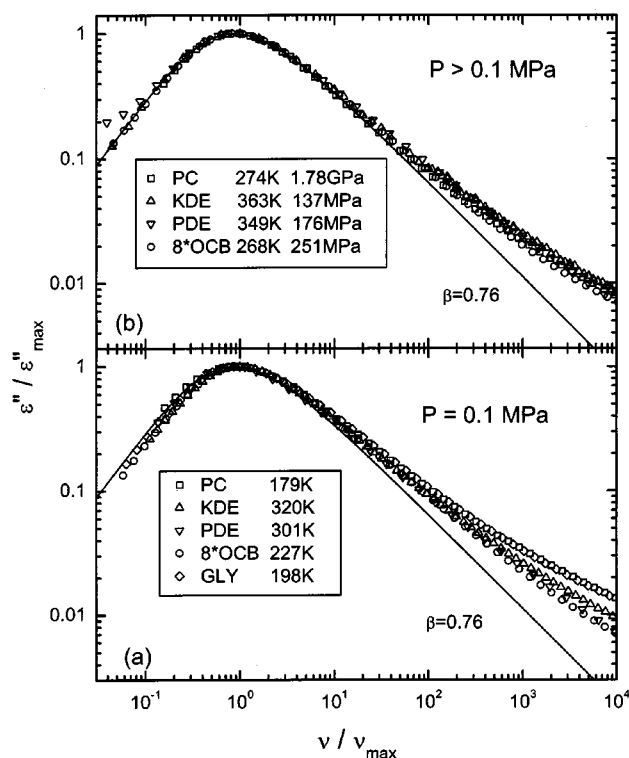


FIG. 1. (a) Superposed dielectric loss spectra at ambient pressure. The measured peak maxima at the indicated temperatures, ν_{\max} (Hz) = 0.15 (PC), 0.090 (KDE), 0.11 (PDE), 0.15 (8CB), and 0.23 (GLY). (b) Superposed dielectric loss spectra at elevated P , with ν_{\max} (Hz) = 0.58 (PC), 1 (KDE), 0.90 (PDE), and 2.0 (8CB). The fit to the KWW function (solid line) yields $\beta = 0.76 \pm 0.04$.

tures and pressures are such that $\tau \sim 1$ s, although the data were shifted slightly to superimpose the peak maxima. This superpositioning demonstrates the near equivalence of the shapes, and extends to higher frequencies for the spectra at elevated pressure, since the contribution from any secondary process is better separated. This can be noted in the data for PC, which deviate at higher frequencies for $P = 0.1$ MPa [Fig. 1(a)], but not at $P = 1.78$ GPa due to weaker contribution from the excess wing [Fig. 1(b)]. These spectra were fit to the transform of the KWW function, with the best-fit value of $\beta = 0.76 \pm 0.04$, independent of pressure. As reported previously, glycerol conforms to the expected correlation between m and β ,¹⁵ while PC is an exception.⁵ Thus, we expect the fragility of the three other liquids to be similar to that of glycerol, and much smaller than m for PC.

The relaxation times at ambient pressure were measured over a range of temperatures, with values of T_g (taken as the temperature at which $\tau = 100$ s) obtained by interpolation or, for PC and 8*OCB, extrapolation of τ by one decade. In Fig. 2, these τ are plotted as a function of the reciprocal temperature normalized by T_g . It is obvious that the curves are quite different, notwithstanding the equivalent shapes in Fig. 1. From the slope at T_g , we obtain values for m which span a very wide range (Table I). Thus, the anomaly previously noted for PC⁵ extends to the other glass-formers, which, excepting glycerol, are all simple van der Waals liquids.

These results also are at odds with the coupling model, which predicts that the breadth of the relaxation function,

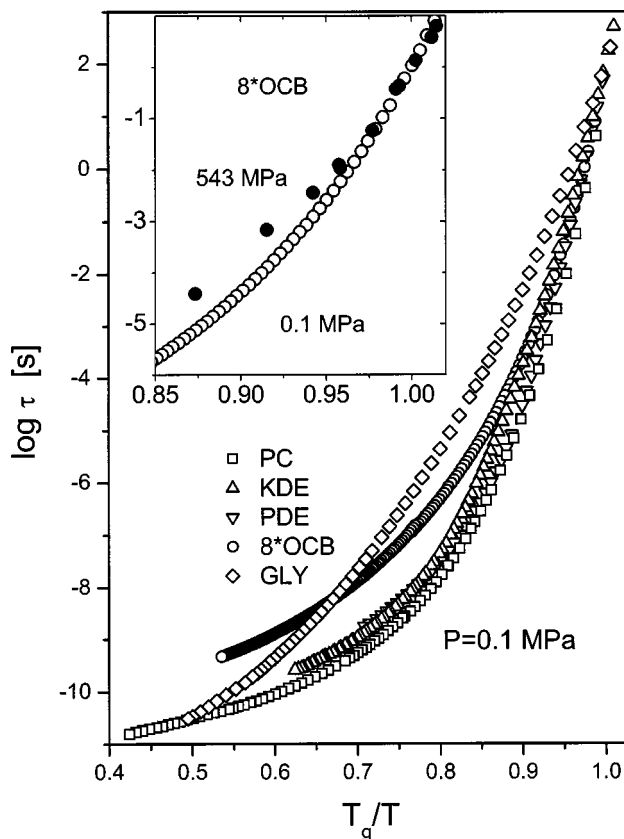


FIG. 2. Arrhenius plots of the α -relaxation times of five glass-formers all having relaxation functions with similar breadths. Temperatures have been normalized by the value at which $\tau = 100$ s. The inset compares the curve for 8CB at ambient and elevated pressures, with T_g taken to be the temperature at which $\tau = 1$ s.

reflecting the strength of the intermolecular cooperativity, is directly correlated with the temperature dependence of the relaxation times.⁶ The departure of the experimental results from the model's prediction may reflect entropic contributions to the local dynamics unaccounted for by the model.¹⁶

Since an increase in hydrostatic pressure does not alter the shape of the relaxation function for these liquids (when compared at equal τ), the expectation is that their fragility will not change with pressure. In the inset to Fig. 2 are shown the relaxation times for 8*OCB, obtained from isotherms measured at ambient and elevated pressures. These τ are plotted versus the inverse temperature normalized by the temperature at which $\tau = 1$ s. (Note that 100 s requires too long an extrapolation of the high pressure data. The T_g for 1 s is 227 K at ambient pressure, which is 6 deg higher than for

TABLE I. Glass transition temperatures and fragilities ($P = 0.1$ MPa and $\tau = 100$ s).

| | T_g (K) | m |
|-------|-----------|-----|
| PC | 157 | 93 |
| GLY | 188 | 51 |
| 8*OCB | 221 | 87 |
| PDE | 294 | 75 |
| KDE | 314 | 68 |

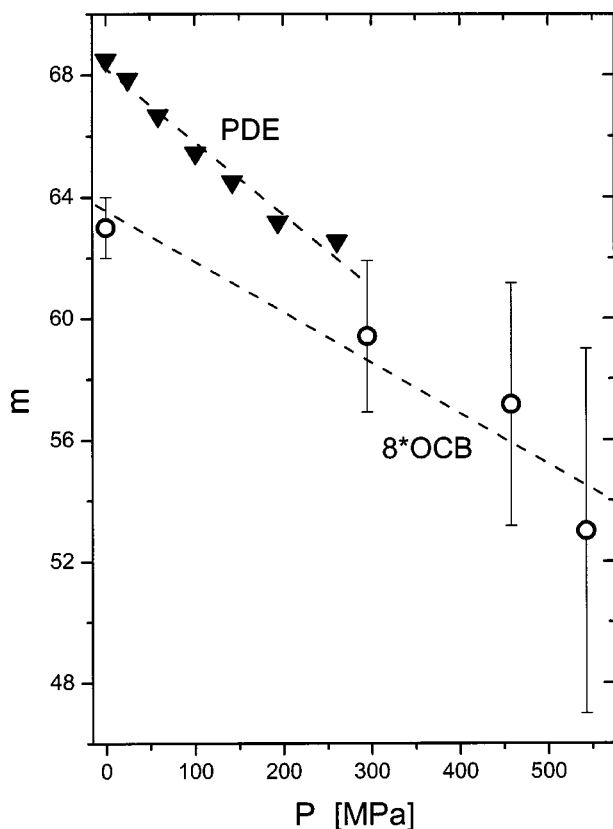


FIG. 3. Pressure dependence of fragility calculated for $\tau=1$ s using Eq. (1). For both liquids, the breadth of the α -relaxation function is invariant to pressure.

$\tau=100$ s, increasing to 363 K for $P=543$ MPa.) The two curves do not superimpose. From the respective slopes at T_g , m for 8*OCB decreases from 63 at $P=0.1$ MPa to 53 at $P=543$ MPa.

We can also calculate m using the relation

$$m = T_g \left(\frac{\partial \log \tau}{\partial P} \right)_{T_g} \bigg/ \left(\frac{dT_g}{dP} \right)_{T_g}, \quad (1)$$

where the pressure coefficient of T_g is obtained from isobaric measurements. Sufficient data are available to evaluate the pressure dependence of m for 8*OCB and PDE, again using $\tau(T_g)=1$ s, with the results shown in Fig. 3. For both liquids, pressure reduces the fragility, $dm/dP = -17 \pm 4 \text{ GPa}^{-1}$ for 8*OCB and $-24 \pm 2 \text{ GPa}^{-1}$ for PDE. There is

no corresponding decrease in the breadth of the spectra in Fig. 1. Such departure at elevated pressure from the correlation between β and m is also found for a polymethyltolyl siloxane,¹⁷ salol,¹⁸ and some methoxyphenyls.¹⁹ In each case, pressure reduces m without a concomitant narrowing of the relaxation function. However, for the hydrogen-bonded glass-formers glycerol¹⁵ and polypropylene glycol,^{20,21} the opposite result is obtained: Pressure increases the fragility, without any change in the peak breadth.

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