Ionic conductivity and dielectric relaxation in poly[(phenyl glycidyl ether)-co-formaldehyde]

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Abstract
Ionic conductivity data and structural relaxation times for poly(phenyl glycidyl ether)-co-formaldehyde (PPGE) are compared for the supercooled liquid under a wide range of temperatures and pressures. Conformance to the fractional Debye–Stokes–Einstein (fDSE) relation was observed under all conditions. The fDSE exponent, $=0.81$, provides an estimate of the relative magnitude of the activation volumes for conductivity and dielectric relaxation. The smaller activation volume for the former suggests less free volume is necessary to accommodate ion diffusion in the PPGE than that required for dielectric relaxation. We also fit the combined temperature and pressure dependences of both the conductivity and relaxation times to the Avramov equation.

1. Introduction

The use of hydrostatic pressure is an increasingly popular means of obtaining new insights into glass transition phenomena [1–22]. Pressure is a fundamental thermodynamic quantity, and a material's response to pressure is an essential structure/property relationship. The use of pressure also allows assessment of the relative contributions of thermal activation and free volume to structural relaxation [18, 23, 24].

One aspect of some import to understanding the glass transition is the decoupling of relaxation times and transport coefficients in molecular liquids approaching T_g. This can lead to differences in the effect of temperature on the diffusivity, viscosity, structural relaxation, and conductivity. This decoupling has been related to the heterogeneity (spatial [25, 26] or dynamic [27]) intrinsic to supercooled liquids [28]. Our interest herein is in investigating the effect of pressure on the decoupling of relaxation and ionic conductivity.

To do this we analyse dielectric data for the glass-former poly(phenyl glycidyl ether)-co-formaldehyde (PPGE). This material is especially convenient for this type of study, given its large dipole moment, resistance to crystallization, and convenient glass temperature ($=264$ K).

Previous investigations of the effect of pressure on structural relaxation in PPGE have been reported [4, 11, 29], while Corezzi *et al* [30] used dielectric spectroscopy together with heat capacity and viscosity measurements to analyse the crossover dynamics at ambient pressure. In this paper, we combine dielectric relaxation times reported elsewhere [11, 29] with ionic conductivity measurements. These data cover a broad range of both temperature and pressure in the supercooled liquid state.

2. Experimental details

The PPGE, obtained from Aldrich, had a molecular weight equal to 345 g mol^{-1}. Dielectric measurements employed a Novocontrol Alpha analyser. The sample was contained between parallel plates, separated by a quartz spacer, and mounted within a cylindrical capsule. This cell was sealed and mounted inside a Teflon ring, then placed in a high-pressure chamber. Pressure was measured by a Nova Swiss tensometric pressure meter with a resolution of 0.1 MPa. The temperature was controlled to within 0.1 K by means of a liquid flow from a thermostatic bath.

3. Results and discussion

Figure 1 displays the ionic conductivity, σ, and the structural relaxation time, τ, for PPEG. The two variables respond similarly (inversely) to pressure and temperature. Different motions in a liquid may be coupled, leading to similar timescales and the same temperature dependence. The latter is expressed by the so-called Debye–Stokes–Einstein (DSE) equation [31, 32], which for the ionic conductivity and the dielectric relaxation time is [34]

$$\frac{\sigma \tau T}{c} \approx \sigma \tau = \text{constant} \tag{1}$$

where c represents the concentration of charges. Since neither c nor T changes substantially over the range of most structural relaxation measurements, it is common to plot σ versus τ double-logarithmically, to yield a slope expected to equal minus unity. Although conformance to the DSE relation is attained at sufficiently high temperatures [33, 34], below some characteristic timescale the translational motions are enhanced [35–37]. This requires adoption of the empirical fractional Debye–Stokes–Einstein (fDSE) equation [38–40]

$$\sigma \tau^s = \text{constant} \tag{2}$$

in which s (<1) serves as an adjustable parameter.

In figure 2 we plot the conductivity data from figure 1 versus τ, each data point representing a given temperature and pressure. The least-squares fit of equation (2) yields $s = 0.808 \pm 0.005$. This is within the range of values reported for other epoxy resins [34, 38]. It is noteworthy that the relationship between σ and τ, although deviating from the DSE law, is invariant to hydrostatic pressure up to $P = 213$ MPa. The longest relaxation time in figure 2 is less than 1 ms. At atmospheric pressure, a change in dynamics of PPGE is observed at $\sim 1.16 T_g$, which corresponds to $\tau \approx 10^{-6}$ [30]. This change in dynamics has recently been shown to be governed by the magnitude of the relaxation time, independently of any combination of temperature and pressure [35, 36]; thus, the single relationship in figure 2 is expected.

When the fragility (T_g-normalized temperature dependence) is independent of pressure, combined temperature and pressure dependence times can be described using the Avramov equation [41, 42]. For structural relaxation times this is given by [41]

$$\log \tau = \log \tau_0 + 13 \left(\frac{T_\tau}{T}\right)^\alpha \left(1 + \frac{P}{\Pi}\right)^\beta. \tag{3}$$
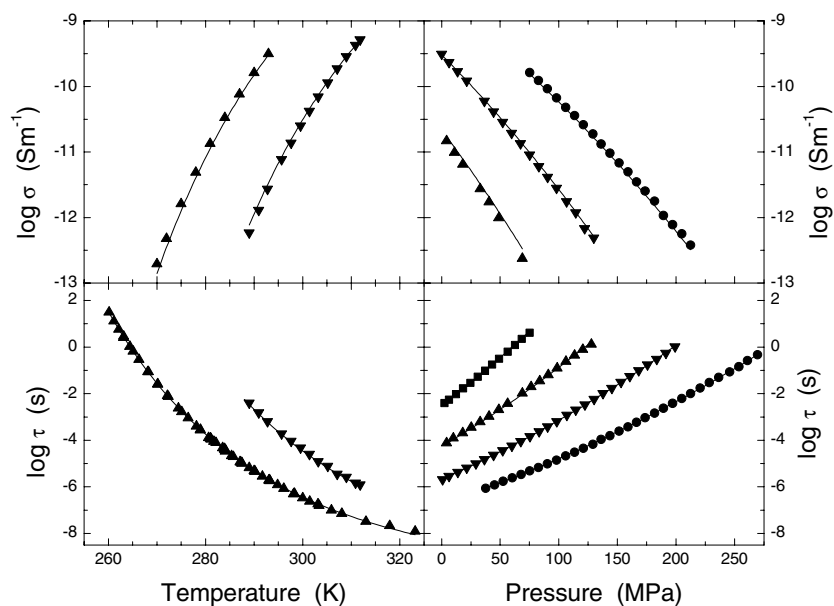
Figure 1. Behaviours of the relaxation times and dc conductivity as a function of temperature at $P = 0.1$ MPa (▲) and 95.5 MPa (▼), and of pressure at $T = 274$ K (■), 283 K (▲), 293 K (▼), and 303 K (●). The solid curve represents a fit to the Avramov equation.
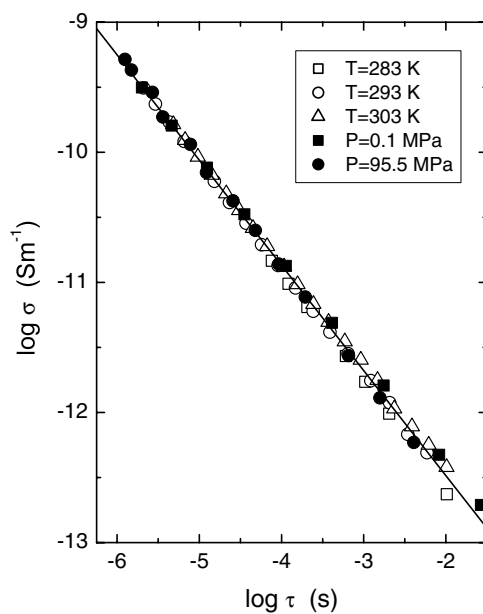
Figure 2. The dc conductivity versus the relaxation time for both the isothermal and isobaric data. The straight line corresponds to equation (2) with $s = 0.81$.

In this equation, τ_0, T_τ, α, Π, and β are material constants. The factor of 13 is an artifact of the original derivation in terms of the viscosity (which for liquids at T_g is approximately 10^{13}

Table 1. Avramov parameters for PPGE (equations (3) and (4)).

	τ	σ
$\log \tau_0 / \log \sigma_0$	-9.95 ± 0.04 (s)	-6.06 ± 0.1 (S m^{-1})
T_τ / T_σ	256.1 ± 0.1 K	249.6 ± 0.2 K
α	8.27 ± 0.06	
Π	439 ± 6 MPa	
β	2.28 ± 0.04	

P) [41], and is maintained herein for consistency with previous works. The Avramov model has been successfully applied to describe $\tau(T, P)$ data for polymethylphenylsiloxane [43], diglycidyl ether of bisphenol A [44], cresolphthalein-dimethylether [1, 7], as well as structural relaxation times over a more limited range than herein for (PPGE) [29]. In favourable cases, the Avramov parameters can be independently deduced from other properties of the material [43, 45, 46]. Otherwise, they are freely adjustable, with equation (3) serving only to parametrize the data.

In fitting the $\sigma(T, P)$ and $\tau(T, P)$ results, we take advantage of the fact that these data conform to the fDSE rule (figure 2). This implies that the response to temperature and pressure is the same; that is, the exponents α and β in equation (3) are the same. If we assume, moreover, that the pressure coefficient Π is the same for σ as for τ, we can write a corresponding expression for the ionic conductivity:

$$\log \sigma = \log \sigma_0 - 13 \left(\frac{T_\sigma}{T}\right)^\alpha \left(1 + \frac{P}{\Pi}\right)^\beta. \tag{4}$$

The reference temperatures for τ and σ are related by

$$s = \left(\frac{T_\tau}{T_\sigma}\right)^\alpha. \tag{5}$$

Thus, we fit the isothermal and isobaric data in figure 1 simultaneously to equations (3) and (4), subject to the constraint specified by equation (5). The results are shown as the solid lines in figure 1, with the best-fit parameters listed in table 1. The agreement with the experimental results, which cover a broad range of conditions, is quite satisfactory. Note that $(T_\tau/T_\sigma)^\alpha = 0.81$, as determined from figure 2.

The pressure dependence of the relaxation times can also be analysed in terms of an activation volume, ostensibly a measure of the free volume necessary for local motion. For the relaxation time, the activation volume is defined as [23]

$$V_\tau^\#(T, P) = RT \left(\frac{\partial \ln \tau}{\partial P}\right)_T \tag{6}$$

with an analogous expression for the dc conductivity [47]:

$$V_\sigma^\#(T, P) = RT \left(\frac{\partial \ln \sigma}{\partial P}\right)_T. \tag{7}$$

Note that $V_\tau^\#$ is usually found to vary with both temperature and pressure. Combining equations (6) and (7) gives [40]

$$s = -\left(\frac{V_\sigma^\#(T, P)}{V_\tau^\#(T, P)}\right). \tag{8}$$

This indicates that $V_\sigma^\# < V_\tau^\#$ for all conditions of T and P. Note that equation (8) can be verified by calculating the activation volumes directly from the $\tau(T, P)$ and $\sigma(T, P)$ data,

using equations (6) and (7) respectively. Within the scatter in calculating the derivatives, the results are consistent with the value of the fDSE exponent. For example, at atmospheric pressure and 283 K, we obtain $V_\tau^\# = 130$ ml mol^{-1} and $V_\sigma^\# = 111$ ml mol^{-1}, which gives 0.85.

4. Conclusions

The decoupling of structural relaxation and ionic conductivity in PPGE was studied under isobaric and isothermal conditions. The experimental data obey the phenomenological fDSE equation, with $s = 0.81$. Note that since each datum in figure 2 represents a given temperature and pressure, the same value of the fractional exponent would be obtained for an analysis at constant-volume conditions. Using the value of s obtained and equation (5), the Avramov equation was applied to satisfactorily describe the T- and P-dependences of the dc conductivity and structural relaxation times, with the same values of α, β, Π for both processes.

The fDSE exponent also gives the ratio of the respective activation volumes for the dc conductivity and structural relaxation. Although the activation volumes vary with both temperature and pressure, we find that $V_\sigma^\# < V_\tau^\#$ for all conditions. This is consistent with the idea that there are smaller space requirements for diffusion of ions within the PPGE, in comparison to the volume associated with reorientational motions of the segments. This is the general expectation for non-spherical structures.

Acknowledgments

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