Pressure and temperature dependence of structural relaxation in diglycidylether of bisphenol A

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The structural (α-) relaxation in diglycidylether of bisphenol A (DGEBA) has been examined using three spectroscopic methods: dielectric spectroscopy (DS), dynamic light scattering–photon correlation spectroscopy (LS), and mechanical spectroscopy (MS). The DS and LS measurements were carried out as a function of both temperature and pressure. Moreover, pressure-volume-temperature measurements were obtained for the DGEBA. These data allow an assessment of the relative contributions of thermal energy and free volume to structural relaxation in DGEBA. The results clearly show a substantial role for both thermal and free volume fluctuations in the dramatic slowing down of the dynamics. The combined temperature- and pressure-dependences of the dielectric and light scattering relaxation times were analyzed using the Avramov equation, implying that the fragility (normalized temperature dependence) is pressure independent over the studied range of pressures. The pressure dependence was the same as measured by the different spectroscopies. Conformance to the time-temperature-pressure superposition principle was also observed for all measurement techniques. © 2003 American Institute of Physics. [DOI: 10.1063/1.1538597]

I. INTRODUCTION

The behavior of supercooled liquids remains of substantial interest in condensed matter physics. Recently, significant progress has been made through the use of pressure as an experimental variable.1–9 A glass former’s response to pressure extends the characterization of structure-property relationships. In particular, measurements of combined temperature- and pressure-dependences of the relaxation and transport properties shed light on the relative importance of temperature and density.10–12

Since models for the dynamics of glass formers invariably focus on either thermal activation13–15 or free volume,16–18 pressure measurements can provide critical tests of theory.

In this paper, we report dielectric, dynamic mechanical, and dynamic light scattering measurements on the diglycidylether of bisphenol A (DGEBA), a commercially significant oligomeric epoxy.19 This material is well-suited for studies of structural relaxation, since it is amorphous and has a convenient glass temperature. A lower molecular weight DGEBA was previously investigated both by dielectric spectroscopy20–22 and dynamic light scattering.23,24 In characterizing the dynamics of supercooled liquids, it can be quite useful to employ more than one spectroscopy, since different probes may weight differently the various molecular motions. In the case of DGEBA, dielectric spectroscopy is sensitive to motion of the polar oxirane moiety, whereas the optical anisotropy governing light scattering arises mainly from the phenyl group. The dielectric and light scattering measurements herein were carried out at elevated hydrostatic pressures. This allows the pressure dependence of various dynamic properties, including the fragility, to be investigated. Moreover, we have also carried out pressure-volume-temperature measurements on the DGEBA. The equation-of-state data allow the relaxation properties to be expressed as a function of density, whereby the relative magnitude of thermal and free volume effects on structural relaxation can be quantified.

Recently, Avramov developed a model to describe the combined effects of temperature and pressure on the relaxation time or viscosity.24 Analysis of experimental data using the Avramov equation yields a determination of the effect of pressure on glass transition temperature. It is worth noting that this model offer an explicit connection to thermodynamic quantities. Herein we parameterize our data using the Avramov equation, and also use it to test the model’s validity.

II. EXPERIMENT

The material used for this study was the epoxy resin, diglycidylether of bisphenol A (DGEBA), from Aldrich. This oligomer, which has the linear structure shown in Fig. 1, is
synthesized by the reaction of bisphenol A with epichlorohydrin. Its number-average molecular weight, $M_n$, is about 1750 g/mol, corresponding to $n=5$.

For ambient pressure measurements, we used a NovoControl GmbH dielectric spectrometer, equipped with a So-latron SI1260 frequency response analyzer and broadband dielectric converter. We measured the dielectric permittivity, $\varepsilon(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega)$, in the frequency range $10^{-2} - 10^6$ Hz. The sample was contained in a parallel plate cell (diameter=10 mm; gap=0.1 mm). Temperature was controlled using a nitrogen-gas cryostat, with temperature stability better than 0.1 K.

For the high-pressure dielectric measurements, we used the Novocontrol Alpha analyser. The capacitor, consisting of two parallel stainless steel plates separated by a quartz spacer, was filled with the sample, then placed in the high-pressure chamber. Pressure was exerted on the chamber via silicone fluid, using a piston in contact with a hydraulic press. The sample capacitor was sealed and mounted inside a Teflon ring to separate the test material from the silicon oil. Pressure was measured by a Nova Swiss tensometric meter (resolution=0.1 MPa). The temperature was controlled within 0.1 K by means of a liquid flowing from a thermostatic bath.

PVT measurements were carried out using a Gnomix instrument, in which the sample is immersed in mercury. A detailed description of the equipment can be found in Ref. 25. Changes in sample volume were measured in the isothermal mode. At a fixed temperature, starting at high temperature, the pressure was increased, up to 200 MPa, with data recorded at various pressures. On completion of measurements along one isotherm, the temperature was decreased and the pressure measurements repeated.

In the dynamic light scattering–photon correlation spectroscopy experiment, an argon ion laser (Model 2020, Spectra Physics, USA), operating at the wavelength of 488 nm, was used at a power of 400 mW. A digital correlator, ALV5000 (ALV GmbH, Germany), was employed to calculate the homodyne correlation functions. Light scattered at an angle of 90° was passed through the analyzer and into an optical fiber. Detection was via a high quantum efficiency avalanche diode detector (High QE Sanderkock). Only the depolarized correlation functions (VH geometry) were measured, since our interest herein is in the reorientational motion.

For the light scattering experiments, high pressure (in the range of 1–160 MPa) was applied by means of nitrogen pressurized with a membrane compressor (Nova Swiss, Switzerland). The sample was contained in a thermostated high-pressure cell. The pressure was determined with a Heise gauge (resolution of ±0.3 MPa). The optical windows of the high-pressure cell were made of fused silica in order to avoid depolarization of the incident and scattered light at high pressure. The temperature was measured with an accuracy of 0.1 °C by means of a thermocouple, placed directly by the sample at beam level. For convenience, the measurements were performed using “constant temperature–scan pressure” cycles, with the same values of pressure applied to facilitate construction of the isobars.

Dynamic mechanical measurements were performed with a Rheometrics RMS 800 spectrometer. Shear deformation using parallel plates (1 mm separation) was applied under stroke control, always remaining in the linear viscoelastic range. The sample was under a dry nitrogen atmosphere during the measurements.

III. RESULTS

A. PVT data

Figure 2 shows the specific volume data for the DGEBA, measured at six hydrostatic pressures. A change in thermal expansivity denotes the transition from the glassy to a liquid state. This transition temperature, $T_g$, is path-dependent, since the material falls out of equilibrium. Above $T_g$, the specific volume conforms to the Tait equation

$$V(T,P) = V(T,0)[1 - C \ln(1 + P/B(T))],$$

FIG. 1. The chemical structure of DGEBA ($n=5$ herein).

FIG. 2. The specific volume measured at pressures equal to (from top to bottom) 10, 40, 80, 120, 160, and 200 MPa. The symbols are the experimental points and the lines represent the fits to Eq. (1). The inset shows the thermal expansivity as a function of pressure, along with the fits to Eq. (8), for $T=333$ K (\(\bullet\); $\kappa_0=5.8 \times 10^{-4}$ K$^{-1}$, $\Pi=292$ MPa) and 363 K (\(\Delta\); $\kappa_0=6.4 \times 10^{-4}$ K$^{-1}$, $\Pi=307$ MPa).
where \( C = 0.0894 \) is a constant. In this equation, the temperature dependence at fixed pressure is described by a quadratic function

\[
V(T,0) = v_0 + v_1 T + v_2 T^2,
\]

while

\[
B(T) = b_0 \exp(-b_1 T).
\]

From simultaneous fitting of all curves in Fig. 2, we obtain

\[
v_0 = 0.685 \text{ ml/g}, \quad v_1 = 3.51 \times 10^{-4} \text{ ml/g C}, \quad v_2 = 6.8 \times 10^{-7} \text{ ml/g C}^2, \quad b_0 = 331 \text{ MPa}, \quad b_1 = 4.46 \times 10^{-3} \text{ C}^{-1}.
\]

The intersection of these fits with the linear expansion of the glass yields the \( T_g \) values shown as symbols in Fig. 3. At low pressures, \( dT_g/dP = 244 \pm 10 \text{ K/GPa} \). At ambient pressure, we obtain \( T_g = 334.9 \text{ K} \) and \( \rho = 1.41 \text{ g/ml} \). For comparison, the glass temperature determined by differential scanning calorimetry (DSC) at a heating rate of 10 K/min was equal to 332 K. This value is consistent with the \( T_g \) data of Koike\(^{19}\) as shown in the inset to Fig. 3.

### B. Dielectric spectroscopy

The dynamics in the vicinity of \( T_g \) were characterized using dielectric spectroscopy. Toward lower frequencies in the dielectric loss, \( \varepsilon''(\omega) \), a conductivity contribution, \( \varepsilon''_{DC} = \sigma_{DC}(\omega \varepsilon_0)^{-1} \) where \( \varepsilon_0 \) is the vacuum permittivity, is present. After subtraction of \( \varepsilon''_{DC} \), the structural relaxation function conforms to the Kohlrausch equation:\(^{27}\)

\[
\text{FIG. 3. The pressure dependence of } T_g \text{ obtained from PVT measurements (•) along with the } T_g \text{ values calculated from Eq. (10) using the parameters obtained from dielectric (---) and light scattering (---) data (Table I) for } T_g(T_p) = 1.27 \text{ s, and } \tau_{G}(T_p) = 11.9 \text{ s. The initial slope yields } 0.244 \pm 0.01 \text{ K/MPa for the pressure coefficient of the glass transition temperature. In the inset are shown the DSC results of Koike (Ref. 19) (□), along with the value for the DGEBA studied herein (■).}
\]

\[
\varepsilon''(\omega) = \int_0^\infty \frac{d}{d\tau} \exp\left(-t/\tau_{DS}\right)^{\beta_{DS}} \sin(\omega t), \tag{4}
\]

in which \( \tau_{DS} \) is the Kohlrausch dielectric relaxation time. The stretch exponents are displayed in Fig. 4. Over this range of \( \tau_{DS} \), any dependence of \( \beta_{DS} \) on \( T \) or \( P \) is less than the experimental scatter; averaging all values yields \( \beta_{DS} = 0.36 \pm 0.02 \). Note that we have expressed results herein for all methods in terms of the physically more meaningful average relaxation time, defined as \( \langle \tau_{DS} \rangle = \tau_{DS} \Gamma(1/\beta)/\beta \), with \( \Gamma(x) \) being the gamma function, with the average values of the \( \beta \) parameter used.

The ionic conductivity and the dielectric relaxation times are related by the Debye–Stokes–Einstein equation (DSE)\(^{28}\)

\[
\frac{\sigma_{DC}(\tau_{DS})}{c} = \text{const.}, \tag{5}
\]

in which \( c \) is the concentration of charges. Since \( c \) and \( T \) change little over the range of structural relaxation measurements, it is common to plot \( \sigma_{DC} \) versus \( \langle \tau_{DS} \rangle \), with the expected slope of unity on double logarithmic scales. However, except at high temperatures,\(^{29}\) the DSE equation must be modified to obtain agreement with experiment. A common empirical alternative is the fractional DSE equation (fDSE)\(^{30}\)

\[
\sigma_{DSC}(\tau_{DS})^{k} = \text{const.}, \tag{6}
\]

in which \( k < 1 \).\(^{31-33}\) The conductivity and relaxation times are plotted in Fig. 5, for the atmospheric pressure measurements. We obtain for the exponent \( k = 0.645 \pm 0.004 \).

The dielectric relaxation times measured at all pressures are plotted in Fig. 6 versus temperature for the isobaric data,
and versus pressure for the isothermal measurements. The fact that the shape of the dielectric relaxation function (reflected in $\beta_{DS}$) is largely invariant to pressure (Fig. 4) implies that the temperature dependence of the relaxation times will also be independent of pressure (given the usual correlation between the stretch exponent $\beta_{DS}$ and the slope of the $T^*$-normalized temperature dependence of relaxation times.\textsuperscript{34–36} Thus we can fit $T_{DS}$ for both the isobars and isotherms simultaneously to the Avramov equation\textsuperscript{24,37}

$$\tau = \tau_o \exp \left( 30 \left( \frac{T_R}{T} \right)^{z_T} \left( 1 + \frac{P}{\Pi} \right)^{z_P} \right).$$

where $\tau_o$, $T_R$, $z_T$, $\Pi$, and $z_P$ are material parameters.\textsuperscript{38} In principle, this entropy-based model offers a connection to thermodynamic quantities.\textsuperscript{24,39} The parameter $z_T$, a measure of the system’s fragility (assumed to be invariant to pressure in this model), is defined as $z_T = 2C_p/(Z\rho)$, where $C_p$ is the heat capacity, $Z$ the degeneracy of the system, and $\rho$ the molar constant. Parameter $z_p$ characterizing the pressure dependence of the dynamics is given by $z_p = 2\kappa_0V_m\Pi/(Z\rho)$, where $\kappa_0$ is the volume expansion coefficient, $V_m$ the molar volume of the system, and $\Pi$ is defined below. Note also that the Avramov model assumes that the cooperative motions engendered by structural relaxation are thermally activated, without consideration of any explicit effects due to volume. In fact, as shown below, volume exerts a significant influence on the relaxation behavior.

Among the parameters appearing in Eq. (7), only $\Pi$ can be estimated from independent measurements. To a good approximation, $\Pi$ can be expressed in terms of the volume expansion coefficient, $\kappa(P) = V_0(P)^{-1}(\partial V/\partial T)$, where $V_0(P)$ is the volume of the liquid at 25 C. The relation is\textsuperscript{34}

$$\kappa(P) = \kappa_0\Pi/(\Pi + P),$$

where $\kappa_0$ is the thermal expansivity at zero pressure. The thermal expansivity can be calculated from the Tait equation fit to the PVT data in Fig. 2:

$$\kappa(P) = V_0(P)^{-1} \left( v_1 + 2v_2T \right) \left( 1 - C \ln \left( 1 + \frac{P}{B(T)} \right) \right) - V(T) \left( \frac{C_bP}{B(T) + P} \right).$$

A weak dependence of $\kappa(P)$ on temperature can be observed in the inset to Fig. 2. At 363 K, $\Pi = 307$ MPa. Using this value, we obtain the fits to the dielectric relaxation times shown in Fig. 6, with the Avramov parameters listed in Table I. It can be seen that the pressure dependence of the relaxation times is in good accord with the expansivity data results. Using the ratio $z_T/z_p = C_p/(\kappa_0V_m\Pi)$ of the fitted parameters and taking $\kappa_0 = 5.8 \times 10^{-4}$ K$^{-1}$ and $V_m = M/\rho = 1241$ ml/M, we estimate the heat capacity $C_p = 915$ J/(M K), equivalent to 0.523 J/(g K). This is a factor of 3 smaller than the value reported for a lower molecular weight DGEBA.\textsuperscript{40}

\begin{table}[h!]
\centering
\caption{Avramov parameters [Eq. (7)].}
\begin{tabular}{llll}
\hline
  & DS & LS & MS \\
\hline
$\log \tau_o$ [s] & $-8.23 \pm 0.05$ & $-6.74 \pm 0.35$ & $-8.87 \pm 0.05$ \\
$T_R$ [K] & 322.2 \pm 0.2 & 320.4 \pm 0.2 & 323 \pm 3 \\
$z_T$ & & 11.4 \pm 0.4 & \\
$\Pi$ [MPa] & & 307 & \\
$z_P$ & 2.75 \pm 0.2 & & \\
\hline
\end{tabular}
\end{table}
The temperature dependence of structural relaxation is used, defined as the temperature at which the relaxation model, such pressure independence is not a general feature of glass formers. 36 Commonly in describing Eq. (7), we can express the glass transition temperature as

\[ T_g(P) = T_R \left( \frac{30 \log e}{\log \left( \frac{\tau}{\tau_\gamma} \right)} \right)^{1/\eta_T} \left( 1 + \frac{P}{\Pi} \right)^{-z_P/\eta_T}. \]  

The pressure dependence of \( T_g \) obtained from PVT measurements can be described by Eq. (10) using the parameters obtained from fitting the dielectric data (Table I), and taking \( \tau_{DS}(T_g) = 1.3 \) s, as shown by the dashed curve in Fig. 3.

The temperature dependence of structural relaxation times is commonly assessed as the fragility (or steepness index), \( m = d \log (\tau)/d(T/T_i) \). In terms of the Avramov model, \( m = z_T \log (\tau/T_\gamma) \), and is independent of pressure. Such pressure independence is not a general feature of glass forming liquids. However, for DGEBA, \( m \) is not a function of \( P \), whereby the Avramov analysis can be utilized. For the dielectric data, we obtain \( m_{DS} = 96 \pm 5 \); thus, DGEBA is a fragile glass former. Commonly in describing relaxation data, a dynamic glass transition temperature, \( T_a \), is used, defined as the temperature at which the relaxation time equals an arbitrary constant, such as 10 s. Introduction of \( T_a \) allows a comparison of results obtained from different techniques. This quantity is related to the Avramov parameter \( T_R \) as

\[ T_a = T_R \left[ \frac{30 \log e}{\log \left( \frac{\tau(T_a)}{\tau_\gamma} \right)} \right]^{1/\eta_T}. \]  

For \( \tau(T_a) = 10 \) s, \( T_a = 332 \) K. Calculating the fragility at \( T_a \), we find \( m_{DS} = 106 \pm 8 \). These results are collected in Table II.

### C. Dynamic light scattering

Dynamic light scattering spectra were measured for the DGEBA at various pressures and temperatures. The obtained correlation functions were also fitted to the Kohlrausch function

\[ g^{(1)}(t) = A \exp \left( -t/\tau_{LS} \right)^{\beta_{LS}}, \]  

where \( A \) is a constant. The best-fit values of the stretch exponent for all temperatures and pressures are shown in Fig. 4. The mean \( \beta_{LS} = 0.38 \pm 0.02 \) is essentially independent of temperature and pressure.

The mean correlation time \( \langle \tau_{LS} \rangle \) was calculated as before. These values are displayed in Fig. 7. In fitting the experimental relaxation times to Eq. (7), we assumed that \( z_T \) and \( z_P \) had the same values as obtained from fitting the dielectric relaxation times. The parameter \( m_{LS} \) is again taken from the PVT data using Eq. (8). The resulting fits of the Avramov equation are included in Fig. 7, with the best-fit parameters listed in Table I. Comparing the parameters obtained from different methods, only the values of \( \tau_\gamma \) differ substantially.

Similarly to the dielectric data, using \( \langle \tau(T_g) \rangle \) as a variable, we again fit Eq. (10) to the glass transition temperatures obtained from the PVT measurements. The results are shown in Fig. 3, with \( \langle \tau_{LS}(T_g) \rangle = 12 \) s. The fragility at this temperature is \( m_{LS} = 90 \pm 6 \). At the dynamic glass temperature, \( T_a = 335.2 \) (for which \( \langle \tau_{LS} \rangle = 10 \) s), we find \( m_{LS} = 89 \pm 10 \). A comparison with the dielectric results is given in Table II.

### D. Mechanical results

The dynamic shear modulus of DGEBA was measured at ambient pressure and various temperatures. The frequency dependencies of the storage \( (G' \) and loss \( (G'') \) moduli exhibit two relaxation modes. The \( \alpha \)-process is visible at higher frequencies, whereas at about three decades lower in frequency, the normal mode, reflecting chain motions, is evident. Herein we focus only on the \( \alpha \)-relaxation. The shape of the \( \alpha \)-relaxation peak is invariant to temperature, with a stretch exponent \( \beta_{DM} = 0.37 \pm 0.02 \). For polymers, a breakdown of the time-temperature superposition principle is the norm for mechanical data extending from Newtonian flow \( (G'' \approx \alpha) \) at low frequencies to the glassy response at the highest frequencies. 46–48 Results for small molecule glass

### Table II. Comparison of dynamics measured by different spectroscopies.

<table>
<thead>
<tr>
<th>Spectroscopy</th>
<th>( \tau(T_g) ) [s]</th>
<th>( m(T_g) )</th>
<th>( T_a ) [K]</th>
<th>( m(T_a) )</th>
<th>( \alpha_{T=1} ) [K (^{-1})]</th>
<th>( \alpha_\gamma/\alpha_\rho )</th>
<th>( E_\gamma/H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric spectroscopy</td>
<td>1.3</td>
<td>96 ± 5</td>
<td>332</td>
<td>106 ± 8</td>
<td>1.6 × 10(^{-3})</td>
<td>1.8</td>
<td>0.62</td>
</tr>
<tr>
<td>Dynamic light scattering</td>
<td>12</td>
<td>90 ± 6</td>
<td>335</td>
<td>89 ± 10</td>
<td>1.3 × 10(^{-3})</td>
<td>1.5</td>
<td>0.58</td>
</tr>
<tr>
<td>Mechanical spectroscopy</td>
<td>0.50</td>
<td>98.5 ± 5</td>
<td>331</td>
<td>113.5 ± 7</td>
<td>\cdots</td>
<td>\cdots</td>
<td>\cdots</td>
</tr>
</tbody>
</table>
formers are more limited.\textsuperscript{11,49,50} The thermorheological simplicity of the present data allows time-temperature superpositioning of the storage, $G'$, and loss, $G''$, moduli, yielding the master curve shown as an inset to Fig. 8. Only shifts along the frequency axis were performed, yielding the temperature dependence of the shift factors, $a(T)$. The mechanical relaxation times were obtained by fitting the master curve of the $G''(\omega)$ spectrum to the Kohlrausch function,\textsuperscript{27} then using the time-temperature shift factors, $a(T)$. The obtained $\tau_{DM}$ are displayed in Fig. 8. For consistency with the analyses of the dielectric and light scattering spectra, we fit the $\langle \tau_{DM} \rangle$ to Eq. (7), yielding the parameters listed in Table I. As seen by the equivalent values of the Avramov parameters, the magnitudes, as well as the temperature dependences, of $\tau_{DM}$ and $\tau_{DS}$ are almost equal. These relaxation times are included in Fig. 8, along with the dielectric and light scattering data at ambient pressure. The $\langle \tau_{LS} \rangle$ deviate from the corresponding results from mechanical and dielectric spectroscopy, in a fashion similar to that found for a lower molecular weight DGEBA.\textsuperscript{23}

Using the Avramov equation to interpolate the data, we find that the mechanical relaxation time, $\langle \tau_{DM} \rangle = 0.5$ s at the ambient pressure $T_g (=334.9$ K from Fig. 3). The respective steepness indices, $m(T_g) = 98.5 \pm 5$ and $m(T_a) = 331$ K $= 113.5 \pm 7$, are consistent with the values of $m$ determined by dielectric and dynamic light scattering spectroscopies. These results are tabulated in Table II.

### IV. DISCUSSION

Recently, different authors\textsuperscript{19,28,30–33} discussed the phenomenon of coupling/decoupling, found in both low molecular weight glass forming liquids and polymers, between the ionic conductivity ($\sigma$) and the $\alpha$-structural relaxation time ($\tau$). It was postulated that in a number of materials the relationship between $\sigma$ and $\tau$ could be expressed by means of the fractional Debye-Stokes-Einstein (fDSE) equation [Eq. (6)]. Koike\textsuperscript{19} examined the effect of molecular weight on the value of fractional exponent $k$ in oligomers of DGEBA. He found that $k$ decreases with molecular weight, revealing greater mobility differences between the two moving units; i.e., the ion charge carrier and the chain segment. In this case, the exponent $k$ can be a useful indicator of the degree of polymerization, especially since $k$ is practically insensitive to the concentration of the ions (e.g., Na$^+$ and Cl$^-$).

In this work, we show that fDSE is also applicable for the DGEBA studied herein ($n = 5$). The enhancement of orientational relaxation is evident in the plot of the conductivity versus $\tau_{DS}$ (Fig. 5), which yields 0.65 for the fractional DSE exponent. This is consistent with data reported by Koike.\textsuperscript{19} From measurements on a substantially lower molecular weight epoxy, Corezzi et al.\textsuperscript{30} observed proportionality between $\sigma$ and $\tau_{DS}$. This is also consistent with the inverse
molecular weight dependence of the exponent $k$ for DGEBA oligomers reported by Koike.\textsuperscript{19} As we mentioned above it has been ascribed to mobility differences between an ion and polymer segments;\textsuperscript{51} however, more work is required to fully understand this effect.

Interpretations of structural relaxation properties are usually based on one of two diametrically opposed concepts, that an accumulation of sufficient local free volume engenders local motion,\textsuperscript{16–18} or that the process involves thermally activated transport over potential barriers.\textsuperscript{13–15,52} Experimental studies restricted to measurements of the effect of temperature cannot resolve this issue; the use of pressure as a variable is required.

In Figs. 9 and 10, we plot the respective dielectric and light scattering relaxation times as a function of density. The latter was determined from the data in Fig. 2, using the Tait equation for interpolation\textsuperscript{52} although some extrapolation was required for densities exceeding 1.42 g/ml. Clearly, for both spectroscopies, the relaxation times are not a unique function of the density or of temperature. Variations of pressure and temperature both can change the relaxation time by more than five decades.

Based on viscosity measurements on glycerol and some other liquids, it has been suggested that for fragile glass formers, temperature is the dominant control variable.\textsuperscript{10} DGEBA is very fragile (Table II), yet Figs. 9 and 10 reveal a strong dependence of the relaxation times on density. Naoki et al.\textsuperscript{5} has ascribed temperature-controlled dynamics to the presence of hydrogen bonding. DGEBA is a normal, unassociated liquid, and thus reveals dynamics controlled by both temperature and volume effects. Similarly, for cresolphthalein-dimethylether, for which $m = 73$, the effects of temperature and volume are quite comparable.\textsuperscript{11,12} Positron annihilation lifetimes, which are a measure of the unoccupied volume, have recently been shown to exhibit a temperature dependence above $T_g$ which correlates with fragility.\textsuperscript{53} These results suggest that the volume concepts cannot simply be ignored when analyzing the dynamics in the supercooled regime.

The results in Figs. 9 and 10 show that the density change for a given change in relaxation time is smaller for pressure than for temperature. Of course, this is expected, since temperature affects both density and thermal energy. Further analysis is required to accurately assess the dependence of the relaxation times on these two variables.

One means to quantify the relative importance of temperature and pressure is from a comparison of the coefficient of isobaric expansivity, $\alpha_p = -\rho^{-1}(\partial \rho / \partial T)_p$, to the coefficient of isochronal expansivity, $\alpha_T = -\rho^{-1}(\partial \rho / \partial T)_T$.\textsuperscript{10} The magnitude of the ratio $|\alpha_c/\alpha_p|$ reflects the role of temperature as a control variable. Using the Avramov fits to the relaxation data, we calculate the temperature and pressure associated with $\tau = 1$ s, with $\alpha_{\tau=1}$ then calculated from Eq.

![FIG. 10. The variation of the dynamic light scattering relaxation times with mass density, for measurements at varying temperatures and ambient pressure (m) and for varying pressures at the indicated temperatures in Kelvin (C). The density at $T_g$ and atmospheric pressure was 1.41 g/ml.](image1)

![FIG. 11. Dielectric relaxation times calculated for a constant volume (dotted lines) equal to 0.01 (A), 0.0125 (O), 0.015 ( ), 0.0175 ( ), and 0.02 (V) ml/g, and at constant pressure (solid line). The inset shows the ratio of the activation energy at constant volume to the enthalpy change at constant pressure. The mean value, $\alpha=0.62$, is indicated by the dotted line.](image2)
The value of $\alpha_P = 8.65 \times 10^{-4} \text{ g m}^{-1} / \text{K}$ for $P = 0.1 \text{ MPa}$ is obtained directly from Eq. (1). These results, listed in Table II, support the inference from Figs. 9 and 10 that neither temperature nor density governs the dynamics.

An alternative approach to assessing the contribution of thermal and free volume effects is from the relative magnitudes of the activation energy at constant volume, $E_V \propto (R \ln \frac{\partial \ln \tau}{\partial T})_V$, and the activation enthalpy at constant pressure, $H \propto (R \ln \frac{\partial \ln \tau}{\partial P})_T$. The ratio $E_V / H$ provides a measure of the contribution of thermal energy to the temperature dependence of the relaxation times.

We calculate these quantities for atmospheric pressure; thus, $H$ is obtained from the slope of the atmospheric pressure data in Figs. 6 and 7. To determine $E_V$, we calculate the relaxation times at fixed volume, by taking vertical intersects of the data in Figs. 9 and 10. The obtained isochoric relaxation times are shown in Figs. 11 and 12 (dielectric data) and 12 (light scattering). The respective slopes at the intersection with the $P = 0.1 \text{ MPa}$ data (shown as solid lines) yield $E_V$ and $H$, respectively. The ratio of these quantities is displayed in the insets to the figures. The average values are $E_V / H = 0.62$ and 0.58 for dielectric and light scattering spectroscopies, respectively. These are consistent with the other results in Table II, indicating a significant role of both thermal energy and volume in determining the structural relaxation times of DGEBA near $T_g$ at ambient pressure. The apparent trend of the ratio $E_v / H$ seen in the inset of Fig. 12 seems to indicate that the importance of volume increases on approaching the glass transition; however, the large error precludes any definitive statement.

Finally, we consider an alternative approach to the analysis of the pressure dependence of relaxation times. If, contrary to the data in Table II, the assumption of a volume activated process is made, then the following expression is obtained,

$$\tau = \tau_0 \exp \left( \frac{p V^d}{RT} \right),$$

where $R$ is the gas constant and $V^d$ represents an activation volume. The latter is ostensibly a measure of the free volume necessary for local motion. The fact that rarely is $V^d$ found to be independent of either pressure or temperature supports our conclusion that free volume is not the dominant control variable for structural relaxation. Nevertheless, we calculate $V^d(T, P) = RT(\partial \ln \pi \partial P)_T$ for both the dielectric and light scattering data, with the results displayed in Fig. 13. When compared at the same temperature, the magnitudes and pressure-dependencies for the two spectroscopies are quite close. Only at the highest pressures is there a suggestion that $V^d_{DS} > V^d_{LS}$.

At ambient pressure the activation volume increases with decreasing temperature, from $V^d = 50 \text{ ml/mol}$ at 390 K to 350 ml/mol at 330 K. This is the usual behavior for glass...
V. SUMMARY

The dynamics of DGEBA, an oligomeric epoxy having a degree of polymerization equal to 5, was studied as a function of temperature and pressure using three different spectroscopies. Although the dielectric and light scattering measurements accentuate different parts of the DGEBA molecule, and the relaxation times per se are different, the results from the other methods. However, at least at atmospheric pressure, the temperature dependence of the mechanical relaxation times was equal to within the experimental error.

For all three spectroscopies, time-temperature superpositioning was valid, and for the dielectric and light scattering measurements, this invariance of the relaxation function extended to pressure. The fragility was invariant to pressure, enabling the combined temperature- and pressure-dependencies to be parameterized using the Avramov equation.

An especially significant determination herein is that thermal energy and density exert a comparable influence on structural relaxation in DGEBA. This implies that theories focusing exclusively on either variable can be misleading.

Models in which intermolecular barrier heights are related to the local density may offer a more realistic approach to understanding the highly cooperative dynamics near the glass transition.

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FIG. 14. Activation volumes, calculated from Avramov model using the parameters listed in Table I, at the indicated temperatures and corresponding pressures for which \(\langle \tau \rangle = 10 \, s\).

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More precisely, the factor of 30 in the Avramov equation is equal to \( \ln\left( \frac{\pi(T_j)}{\pi_n} \right) \) which in the case of low molecular weight liquids is about 13 orders of magnitude \( \approx 30 \). We retain it herein to be consistent with previous publications.


