Relaxation Dynamics of Poly(methyl acrylate) at Elevated Pressure

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ABSTRACT: Dielectric relaxation and complex heat capacity were carried out on high molecular weight poly(methyl acrylate) (PMA). The temperature was found to exert a stronger effect than density on the segmental dynamics, as reflected in the magnitudes of the scaling exponent, $2.55$, and the ratio of isochoric and isobaric activation energies, $0.67$. The dispersion of the heat capacity and dielectric loss were used to obtain estimates of the number of dynamically correlated segments. In accord with prior results on molecular liquids and from simulations, the extent of the dynamic correlations in PMA depends only on the relaxation time. This behavior differs from that of the fragility, which decreases with pressure, showing the disconnect between dynamic heterogeneity and fragility.

INTRODUCTION

A fascinating aspect of the dynamics of supercooled liquids and polymers is the degree to which the reorientational or segmental relaxation time, $\tau_\alpha$, governs various properties. The shape of the relaxation peak, commonly reflected in the Kohlrausch stretch exponent, $\gamma$, and the state points associated with the dynamic crossover, $T_\gamma$ and the dynamic correlation volume, $V_\gamma$, for many glass formers depend only on the relaxation time, independently of temperature and pressure. Similarly, the phase transitions of liquid crystals usually transpire at a fixed value of $\tau_\alpha$. There is also a scaling relation that superposes $\tau_\alpha$ measured at various temperatures and pressures, whereby any combination of temperature, $T$, and density, $\rho$, yielding a given value of $T/\rho^{\gamma}$, where $\gamma$ is a material constant, will have the same relaxation time.

Herein we examine the conformance of poly(methyl acrylate) (PMA) to these general properties. Acrylate and methacrylate polymers have been the subject of many investigations, due both to their commercial significance and to their unusual dynamics. When the pendant alkyl group in methacrylates is large, the polymers exhibit a very broad or even two glass transitions, and these materials often have unusually intense, multiple secondary relaxations. Acrylates commonly serve as the backbone for liquid crystalline polymers. PMA has the smallest repeat unit among acrylate polymers, which simplifies the relaxation behavior. Moreover, the effect of pressure on the fragility of PMA is among the highest reported for any polymer, which makes it an obvious choice to study the effect of pressure on relaxation properties. Despite the diminutive chain units, we observe two secondary relaxation processes, and the properties of the primary structural relaxation in PMA deviate from some of the general behaviors mentioned above.

EXPERIMENTAL SECTION

Poly(methyl acrylate) ($M_\text{w} \sim 4 \times 10^4$ D) was obtained from Aldrich as a toluene solution. (The molecular weight distribution is unknown; however, it has been shown that polydispersity negligibly affects $T_\gamma$ and the shape of the relaxation function.) There is a small effect on the temperature dependence of the relaxation times. The polymer was precipitated by addition of excess methanol, followed by vacuum drying at 323 K for more than 2 weeks. The relaxation behavior is very sensitive to small quantities of residual solvent, so that several additional weeks of drying under vacuum at 335 K were necessary to achieve invariance of the dielectric relaxation spectra, which confirmed that all solvent had been removed.

For the dielectric measurements the PMA was contained between parallel, 16 mm diameter plates, which served as electrodes. The dielectric permittivity was measured using a Novocontrol Alpha Impedance Analyzer and an Imass Time Domain Analyzer. For the measurements at atmospheric pressure, the sample was under vacuum in a closed cycle helium cryostat (Cryo Inc.), with temperature controlled to $\pm 0.02$ K. For high pressure measurements the capacitor cell was inside a pressure vessel (Harwood Engineering Inc.), with an electrically insulating oil used to transmit the pressure. The cell was isolated from the fluid by flexible Teflon and rubber seals. Pressure was applied with a manual pump in combination with an intensifier, and measured using a Sensotec transducer and Heise mechanical gauge (70 kPa accuracy). The high pressure vessel was inside a Tenney environmental chamber, with temperature controlled to within 0.1 K.

Modulated differential scanning calorimetry (MDSC) was performed using a TA Q100 calorimeter. Samples were cooled from the glass transition at a rate of $q = 0.5$ K/min, with temperature modulation 1 K and modulation periods of $T_\text{m} = 40, 60, 90$, and 120 s. The heat capacity was calibrated for each modulation period using a sapphire sample. The error in the MDSC measurements due to the temperature dependence of the heat capacity at the glass transition (nonstationary thermal response) can be estimated from the relative change of the heat capacity, $\Delta c_P/c_P^0$, over one modulation period. This is given by $\Delta c_P/c_P^0 \approx (\Delta c_P^0/d(T)qT_\text{m})qT_\text{m}$ and for the measurements reported herein we estimate $\Delta c_P/c_P^0 \leq 0.02$.

RESULTS AND DISCUSSION

Dielectric Measurements. Representative dielectric spectra of PMA at atmospheric pressure are shown in Figure 1. Three relaxation processes are evident, the $\alpha$ transition (local segmental
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The β process is obscured by other, more intense relaxation peaks. The weak β process is indicated. The contribution of the three relaxations are shown by the fitted curves (dotted lines for −26.9 °C and solid lines for −6.0 °C).

Figure 1. (a) Dielectric loss of PMA at atmospheric pressure and various temperatures. The β process is obscured by other, more intense relaxation peaks. (b) Dielectric loss of PMA at atmospheric pressure and two temperatures below Tg. The weak β process is indicated. The contribution of the three relaxations are shown by the fitted curves (dotted lines for −26.9 °C and solid lines for −6.0 °C).

The β process is close to but faster than the α relaxation, reminiscent of a Johari–Goldstein (J–G) process, determination of its relaxation time has a large uncertainty due to the relatively weak dielectric strength. Also for this reason we could not assess its properties in terms of those expected for a J–G relaxation. The latter has been observed, for example, in poly(methyl methacrylate) (PMMA); 33 a discussion of the β process in other acrylates and methacrylates is presented at the end of this section. The relaxation times of both secondary relaxations exhibit Arrhenius behavior (Figure 2), with activation energies below Tg equal to 80 ± 20 and 38.0 ± 0.4 kJ mol−1 for the β and γ processes, respectively. Certainly for the γ process this activation energy is too small to be a J–G relaxation, indicating that the underlying motion probably involves noncooperative rearrangements of only some atoms in the repeat unit of PMA.

The α process shows the usual non-Arrhenius behavior, with an effective activation energy increasing with decreasing temperature. At the lowest measured Tα (17.2 s), the effective activation energy is 660 kJ mol−1, which corresponds to a steepness index, m = \( \theta \log(\tau)/\partial(T/T_g) |_{T=T_g} \) equal to 118+/- 3. (This choice of Tα avoids extrapolation, reducing the error in the determination of m.) Thus, PMA is one of the more fragrant amorphous polymers. Only polystyrene (vinylethylene) (m = 140) and poly(vinyl chloride) (m = 160) have steeper Tα-normalized Arrhenius slopes. 35,36 (Cross-linking increases the steepness index and can yield even higher values of m.) The peak breadth is generally anticorrelated with m, and for PMA we find \( \beta_{KWW} \) in the range 0.37–0.41 (Figure 3). According to the general pattern for polymers, 39 this \( \beta_{KWW} \) gives a rough estimate of m ~ 115, which is consistent with the present result. From mechanical measurements on PMA, m = 106 and \( \beta_{KWW} = 0.41 \) at \( T_g = 287 \) K. 40 These values are close to our dielectric results, although differences are inherent to the two spectroscopies.

Heat Capacity Measurements. The real and imaginary parts of the heat capacity (modulation period = 60 s) are shown in Figure 4. 43,44 The breadth (fwhm) of the C′′(T) transition interval, 2\( \delta T \), was determined by fitting a Gaussian function to the peak. The values of \( T_g \) and \( \delta T \) for the four modulation periods are listed in Table 1. Defining the relaxation time as \( \tau^* = (2\pi f)^{-1} \), where f is the modulation frequency at the temperature of the maximum in C′′(T), we calculated the \( \tau^* \) shown in Figure 5. Also included are the dielectric relaxation times defined in the same manner from isochronal dielectric peaks, \( \epsilon^*(T) \). Note that \( \tau^* \) from the dielectric data are larger than the values from calorimetry. Tα determined from fitting eq 1 to the dielectric spectra, \( \epsilon^*(\omega) \), are also larger than the calorimetric \( \tau^* \) (cf. Figures 2 and 5).

We did not determine \( \partial T \) from the isochronal dielectric measurements because the background loss introduces large error.
For example, a change in the background of 0.1, which is only 6% of the peak maximum, changes the computed breadth by more than 25%. This background is due to the intense γ process, as seen in the isochronal spectra at the lowest temperatures in Figure 6. However, this background intensity introduces negligible error (<0.5%) in the value of the peak maximum.

**Dynamic Heterogeneity.** The intermolecularly cooperative dynamics involves correlations both in time and in space; thus, this dynamic heterogeneity cannot be quantified directly from linear relaxation measurements. However,

Berthier et al.\textsuperscript{45} derived an approximate formula for the number of dynamically correlated molecules, or segments in the case of polymers, by assuming the dynamics are driven mainly by temperature, rather than density, fluctuations. (This assumption is more correct for polymers than molecular liquids,\textsuperscript{1,13}) For relaxations having the Kohlrausch form, the number of correlated segments is\textsuperscript{46}

$$N_c = \frac{R}{\Delta c_p m_0} \left( \frac{\beta_{KWW}}{e} \right)^2 \left( \frac{d \ln \tau_a}{d \ln T} \right)^2$$

(2)

in which Δc_p is the isobaric heat capacity increment at T_0, m_0 is the monomer molecular weight (86 g/mol for PMA), R is the gas constant, and e is Euler’s number. At least near the glass transition, molecular dynamic simulations have shown that the approximate N_c from eq 2 is quite close to the rigorous value determined from the four-point dynamic susceptibility.\textsuperscript{45,47}

The number of dynamically correlated segments calculated from the dielectric measurements is plotted in Figure 7. It is seen that N_c depends only on the relaxation time, independent of T and P. This finding agrees with our earlier results for four molecular glass formers\textsuperscript{6} and for simulated Lennard-Jones particles.\textsuperscript{7} In the investigated range we find that N_c for PMA varies linearly with log τ_a. Note that because the dependence of the heat capacity on pressure is negligible, we used the atmospheric pressure value of Δc_p \textsuperscript{-1} for all five data sets in Figure 7; that is, we assumed Δc_p \textsuperscript{-1} is constant with pressure.

An alternative formula derived by Donth\textsuperscript{48} is similar to eq 2

$$N_0(T) = \frac{RT^2 \Delta c_p^{-1}}{m_0 (\partial T^2)}$$

(3)

Using the heat capacity data in Table 1, N_0 at atmospheric pressure is calculated and shown in Figure 7. Note that in both eqs 2 and 3, the choice of Δc_p \textsuperscript{-1} [(1/c_p)_\text{liq} – (1/c_p)_\text{glass} ≈ Δc_p/ε] \textsuperscript{-2}, rather than (Δc_p) \textsuperscript{-1}, is arbitrary, affecting the absolute magnitude of N_c or N_0, but not their variation with T, P, or τ_a.\textsuperscript{49} From Table 1 Δc_p \textsuperscript{-1}/Δc_p \textsuperscript{-1} ≈ 0.5. The relation\textsuperscript{50}

$$\frac{\partial T}{\delta \ln \tau_a} \approx \frac{1.07T}{\beta_{KWW} (\frac{d \ln \tau_a}{d \ln T})^{-1}}$$

(4)

together with eq 2 gives

$$N_0 = 6.45N_c$$

(5)

This equation is in reasonable accord with the N_0 in Figure 7. Thus, the two methods of determining the number of dynamically correlated segments agree both in magnitude and in their dependence on τ_a.

By assuming that temperature and polarization fluctuations have the same spectral shape, Saiter and co-workers\textsuperscript{51} applied eq 3 to dielectric measurements, with ∂T taken as the temperature spread of the α peak measured at constant frequency. However, the interference from the γ process, discussed above, precluded accurate determination of ∂T in this manner.

**Table 1**

<table>
<thead>
<tr>
<th>modulation period [s]</th>
<th>T_g [K]</th>
<th>V(T_g) [cm³/g]</th>
<th>ρ(T_g) [g/cm³]</th>
<th>2ΔT [C]</th>
<th>C_{p,liq} [J/(g C)]</th>
<th>C_{p,glue} [J/(g C)]</th>
<th>Δc_p [J/(g C)]</th>
<th>Δ(1/c_p) [(g C)/J]</th>
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<td>1.223</td>
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Thermodynamic Scaling. PVT data from the literature were used to determine the equation of state (EoS) for the PMA

\[
V(T, P) = 0.808 \left[ \exp[6.64 \times 10^{-4} T] \right] \\
\times \left[ 1 - 0.0894 \ln \left( 1 + \frac{P}{247.84 \exp[-4.26 \times 10^{-3} T]} \right) \right]
\]

(6)

where \( T \) is in °C. Plotting \( \tau_a \) versus volume (Figure 8) shows that the segmental dynamics do not depend uniquely on \( V \) (or \( T \)). However, for all nonassociated organic liquids and polymers, it has been found that

\[
\tau_a = \mathcal{T}(TV^\gamma)
\]

(7)

where \( \gamma \) is a material constant and \( \mathcal{T} \) is a function. As shown in Figure 9, the segmental relaxation times of PMA conform well to eq 7 with \( \gamma = 2.55 \). In the inset of the same figure is the scaled relaxation time, \( \tau_{\text{PCS}} \), of PMA measured using photon correlation spectroscopy (PCS) by Fytas et al. 53 using the same EOS as for the dielectric data. The PCS data scale quite well for \( \gamma = 2.75 \), which is close to the value of \( \gamma \) of the dielectric measurements. This confirms previous observations that the values of \( \gamma \) determined for different observables (dielectric relaxation, viscosity, etc.) agree reasonably well.

Using the scaling function (eq 7), \( N_c \) can be calculated as

\[
N_c(T, V) = \frac{R}{\Delta\epsilon/\epsilon} \frac{N_a}{m_o} \left( \frac{\beta_{\text{KWW}}}{e} \right)^2 \left( \frac{d \ln \tau_a}{dT V^\gamma} \right)^2 (1 + \gamma \alpha_{\epsilon} T)
\]

(8)

From eq 8 it follows that for \( N_c \) to be a function of \( TV^\gamma \) (or equivalently of \( \tau_a \)), \( \beta_{\text{KWW}} \) should depend only on \( TV^\gamma \), independently of \( T \) and \( P \), and the product \( \alpha_{\epsilon} T \) should be constant.
Figure 9. Scaling plot of the segmental relaxation time of PMA, with $\gamma = 2.55$. The inset is the scaling plot for the relaxation time measured using photon correlation spectroscopy, $\tau_{PCS}$ by Fytas et al.\textsuperscript{53} with the value of $\gamma$ indicated.

For the PMA herein, neither condition is satisfied: $\beta_{KWW}$ is not a function of $\tau_0$ (Figure 3), and $A_0T_0$ decreases from 0.19 at atmospheric pressure to $\sim 0.15$ at the highest pressure (550 MPa). However, because $N_c$ is a function of $\tau_0$, these variations of $\beta_{KWW}$ and $A_0T_0$ evidently compensate each other.

Starting with the Avramov entropy model of the dynamics,\textsuperscript{54} we previously derived a form for the (otherwise unspecified) function $\mathcal{J}$ in eq $7^{55}$

$$\log(\tau) = \log(\tau_0) + \left(\log(e)\frac{A}{TV}\right)^\phi$$

where $\tau_0$, $A$, and $\phi$ are constants. This function requires only one more parameter than, for example, the Vogel–Fulcher\textsuperscript{1} or Avramov equation\textsuperscript{55} used to describe the temperature dependence of $\tau_0$ at constant pressure. Moreover, the parameters in eq 9 are $T$- and $V$-independent; that is, fitting does not have to be carried out individually for each isotherm. The fits of eq 9 to the PMA $\tau_0$ data are shown in Figure 8; $\log(\tau_0) = -7.5 \pm 0.2$, $A = 534 \pm 8$ K cm$^3$/g$^{-\gamma}$, $\gamma = 2.54 \pm 0.01$, and $\phi = 7.6 \pm 0.3$. Previously we pointed out that $\gamma$ and $\phi$ are not independent but show an inverse proportionality.\textsuperscript{56} In Figure 10 these values of $\phi$ and $\gamma$ are plotted, along with those for other materials; the anticorrelation of $\phi$ and $\gamma$ is evident. Thus, the parameter $\phi$ is to some extent redundant, and eq 9 could be rewritten substituting for $\phi$ with a function of $\gamma$.\textsuperscript{57} Although this relationship between $\phi$ and $\gamma$ is strictly empirical, it does indicate that the single parameter $\gamma$ governs the temperature and pressure behavior (e.g., fragility and activation volume) of the segmental dynamics.

A measure of the relative degree to which volume and temperature control the dynamics is the ratio of the isochoric ($E_V$) and isobaric ($E_P$) activation energies. For PMA Williams\textsuperscript{31} reported $E_V/E_P \geq 0.78$, which is larger than one-half, implying temperature is the more dominant control parameter. The value of this ratio can be calculated from the scaling exponent using\textsuperscript{10,58}

$$\frac{E_V}{E_P} = (1 + \gamma \alpha_0 T)^{-1}$$

Unlike $\gamma$, $E_V/E_P$ varies with temperature. From this equation we calculate at $T_0 = 289$ K ($\alpha_0 = 10^4$ s$^{-1}$) $E_V/E_P = 0.67$. This is smaller than the earlier result\textsuperscript{31} possibly because the molecular weight used in the prior study ($2 \times 10^5$ D) was much larger than herein; chain ends accentuate the effect of volume on $\tau_0$,\textsuperscript{11} rendering $E_V/E_P$ smaller.

A general property of nonassociating liquids and polymers is isochronal superpositioning,\textsuperscript{3,4,59} which refers to the invariance of the shape of the relaxation peak to changes in $T$ or $P$, as long as $\tau_0$ is constant. However, for the $\alpha$ process in PMA $\beta_{KWW}$ is almost independent of pressure at constant $T$, which means that at fixed $\tau_0$, the dielectric loss peak becomes narrower with increasing pressure (corresponding to increasing temperature (Figure 3)). This breakdown of isochronal superpositioning in PMA is illustrated in Figure 11. Such behavior has been observed before only for hydrogen bonded liquids, a result of the concentration of H-bonds changing with $T$ and $P$, although in those cases spectra broaden with increasing pressure.\textsuperscript{3,4,60}

However,
where $T_1$ is the temperature at which $\tau_\alpha$ was measured at atmospheric pressure.\textsuperscript{35} Isobars calculated in this manner for six different pressures between 50 and 500 MPa are displayed in Figure 12 in the form of fragility plots. From the linear fit of $m$ vs $P$ we find $dm/dP = -27 \pm 5$ GPa$^{-1}$. This is significantly smaller than the pressure coefficient reported previously from more limited data, $-180$ MPa$^{-1}$.\textsuperscript{36} Nevertheless, the change of fragility with pressure for PMA is among of the largest of all liquids and polymers.\textsuperscript{33}

Because $m$ changes with pressure, but $N_c$ is independent of $P$ at fixed $\tau_\alpha$ (Figure 7), there can be no direct relationship between $N_c$ and fragility. We had previously demonstrated this lack of correlation between these two quantities at atmospheric data for various materials,\textsuperscript{6} at least for PMA, varying pressure shows that $m$ and $N_c$ are uncorrelated even within a single material.

**Comparison with Other Acrylates and Methacrylates.** Although the molecular structures of PMMA and PMA differ only by a pendant methyl group, this affects the chain rigidity and local packing enough to change $T_g$ by more than 100 K. However, the $\beta$ relaxation times for PMMA\textsuperscript{18} (although larger, are relatively close to those of PMA (between one and two decades). Recently, a similar scenario was reported for poly(ethyl acrylate) (PEA) and poly(ethyl methacrylate) (PEMA).\textsuperscript{62} The $\tau_\beta$ for the acrylate polymer is about 1.5 decades faster than for the methacrylate counterpart and has a comparable activation energy. Also, for both PEA and PMA, the dielectric strength of the $\beta$ process is much smaller than that of the $\alpha$ process, with a third, intense process ($\gamma$ process) at much higher frequency. When the relaxation times are normalized to the glass transition (Figure 13), the $\alpha$ and $\beta$ processes are more than 3 decades closer for the acrylates than for the methacrylates.

Schmidt-Rohr et al.\textsuperscript{33} used NMR and MD simulations to determine that the $\beta$ process in PMMA corresponds to flipping of the bulky pendant group. Because of the asymmetry of this side group, its reorientation requires rearrangement of the entire repeat unit. It can be speculated that this flipping of the bulky side group is responsible for the $\gamma$ process in polyacrylates. In PMMA and PEMA the molecular structure constrains this motion, causing it to become cooperative. The weaker intensity and longer $\tau_\beta$ (Figure 13) for the $\beta$ process in the acrylates indicates noncooperative motion of the main chain, consistent with the smaller separation between $\tau_\alpha$ and $\tau_\beta$.

**SUMMARY**

From PVT and dielectric relaxation data at ambient and elevated pressures, and from modulated calorimetry experiments on a high molecular weight PMA, the following results were obtained:

1. A new secondary relaxation was discovered, which is much weaker in dielectric strength than the higher frequency secondary process, and has an activation energy almost 2-fold higher. This process may be the $J-G$ relaxation in PMA, as a comparison with the PMMA relaxation map suggests.
2. The number of dynamically correlated segments was estimated from both dielectric and DSC data, the two methods yielding consistent results. In agreement with previous work on small molecule liquids, the dynamic correlation volume is constant for all state points having a given value of the $\alpha$ relaxation time.
3. Segmental relaxation times for the PMA conform to density scaling. From the scaling exponent $\gamma = 2.55$, the activation energy ratio is calculated. Its magnitude, $E_\gamma/E_\alpha = 0.67$ at $T_g$, indicates a more dominant role of temperature over volume on the structural dynamics.
4. The α relaxation dispersion in PMA deviates from the isochronal superpositioning found for virtually all other nonassociated liquids and polymers. The deviation may be due to overlapping of a secondary process.

5. The fragility of PMA changes strongly with pressure, \( \frac{dn}{dP} = -27 \pm 5 \text{ GPa}^{-1} \), the negative sign of the pressure coefficient in accord with other materials lacking H-bonds. In consideration of item 2 above, this nonzero pressure dependence affirms the lack of correlation between fragility and dynamic heterogeneity.

**Notes**

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