Aging of a low molecular weight poly(methyl methacrylate)

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ABSTRACT

Dielectric relaxation of a low molecular weight PMMA was measured in both the equilibrium and glassy states. The intense β process, due to motion of the pendant ester moiety, exhibits a change in T-dependence of both its relaxation time and dielectric strength at T_g, reflecting the coupling of this high frequency process to the backbone conformational changes underlying the α dynamics. Consequently, we can exploit the change in the properties of the β process during physical aging to quantify the α relaxation time and its T-dependence for glassy PMMA. The obtained values, $\tau_\alpha > 10^4$, are too long for direct measurement.

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1. Introduction

Although the glass transition remains a major unsolved problem in condensed matter physics, most research efforts address the properties of the equilibrium liquid upon approach to vitrification. The glassy state *per se* is equally relevant, but structural relaxation times of a glass are too long ($\tau_\alpha > 10^4$ s) for direct experiments to be feasible. However, an investigation of the glassy state is possible by studying the time evolution of secondary processes which have much smaller relaxation times [1–3]. Recently we showed that the time evolution of the β peak for glassy 1,2-polybutadiene (PB) reflects the structural aging dynamics [4], whereby time constants for property changes during physical aging could be identified with τ_α. We found that the temperature-dependence of τ_α changes from strongly non-Arrhenius in the liquid to Arrhenius in the glassy state, due to the invariance ("freezing") of the structure of the PB below T_g.

In this work we extend the method to polymethylmethacrylate (PMMA). The β process in PMMA has a very large dielectric strength, enhancing the accuracy of the analysis. This strength, as well as the β relaxation time, both change their temperature dependence at T_g, reflecting the strong coupling of the pendant group to backbone motion of the polymer [5]. After quenching into the glassy state, we follow the change in the dielectric β dispersion with time, extracting from the aging kinetics a value for τ_α at various temperatures below T_g. These are compared to the relaxation times measured directly in the equilibrium polymer above T_g.

2. Experimental

The oligomeric PMMA ($M_w = 1970$ D; $M_n = 1720$ D) was purchased from Polymer Standards Service and used as received. The dielectric permittivity was measured using a Novocontrol Alpha Analyzer and an Andeen Hagerling 2700A, the latter mainly for aging experiments. For isobaric measurements the sample cell consisted of two parallel plates with a 55 μm Teflon spacer ($C_g = 50.5$ pF). For the aging experiments the same electrodes were used, but concentricity was maintained with a Teflon ring and there was no spacer to allow for volume changes. For this reason the permittivity values during aging are not exact and we report them in arbitrary units. The sample capacitor was maintained in a closed-cycle helium cryostat under vacuum, with temperature measured by a platinum resistance thermometer mounted in one of the electrodes. The aging experiments were done by cooling the sample from $T = 383$ K ($> T_g$) at a cooling rate of 2 K/min to a temperature well below T_g, and then measuring the evolution of the dielectric spectra over several days. This procedure was carried out for five aging temperatures.

3. Results and discussion

The dielectric loss spectra of PMMA (Fig. 1) above the glass transition temperature, T_g, show three processes, a very intense β-relaxation, a less intense α-relaxation, and DC conductivity due to sample impurities. The relative intensity of the α and β processes depends on chain length [6]. For short chains the α peak is more intense, while for the high molecular weights the situation is reversed. For the molecular weight herein the intensities in the vicinity of T_g are very close, which facilitates deconvolution of the three contributions. In the glassy state the dielectric spectra show a prominent asymmetric β peak, but no other peaks can be clearly resolved.
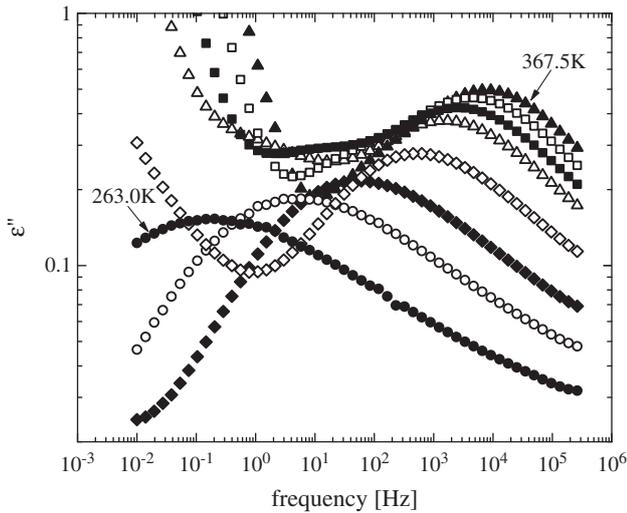
Fig. 1. Dielectric loss spectra for PMMA; from left to right the temperatures are 263.0, 290.5, 312.6, 338.2, 351.5, 357.4, 362.6, and 367.5 K. At higher T a strong σ_{DC} conductivity is evident.

Our analysis assumed the permittivity spectra were a superposition of a Havriliak–Nagami (HN) function[7] to describe the β process, a Kohlrauch–Williams–Watts (KWW)[7] for the α process, and a constant phase element for the DC conductivity

$$\varepsilon^*(\omega) = \frac{\sigma_{DC}}{\varepsilon_0}(i\omega)^{-s} + \Delta\varepsilon_\alpha L_{i\omega}\left[-\frac{d\varphi_\alpha(t,\tau_\alpha)}{dt}\right] + \frac{\Delta\varepsilon_\beta}{\left[1 + \left(i\omega\tau_\beta\right)^a\right]^b} + \varepsilon_\infty$$

$$\text{with}\quad \varphi_\alpha(t,\tau_\alpha) = \exp\left[-(t/\tau_\alpha)^{\beta_{KWW}}\right]$$

(1)

where ε_0 is the vacuum permittivity, τ_α and τ_β are relaxation times, $\Delta\varepsilon_\alpha$ and $\Delta\varepsilon_\beta$ dielectric strengths, a and b shape parameters for the β process ($0 < a$, $b \le 1$), β_{KWW} the stretch parameter of the α process ($0 < \beta_{KWW} \le 1$), σ_{DC} the DC conductivity, and s ($0 < s \le 1$) a parameter describing the deviation from the ideal ($s = 1$) behavior of the conductivity. This deviation we ascribe to the partially blocking nature of the electrodes (i.e., electrode polarization), and the effect was quite small herein, with $0.94 \le s \le 0.96$, decreasing with decreasing T. The Laplace transform of the KWW function, φ_α, was done numerically using the method of McDonald [8] implemented using Grafity software.[9] The parameter β_{KWW} varied only slightly with temperature, changing from 0.381 at high T to 0.379 at low T.

An example of a simultaneous fit of Eq. (1) to the real and imaginary parts of the permittivity is shown in Fig. 2, the three processes indicated as dotted lines. The uncertainty of the fitting is larger at higher temperature because the α and β processes are closer and the α process weaker; thus, we restricted our analysis to temperatures for which the separation was more than two decades.

Arrhenius plots for τ_α and τ_β are shown in Fig. 3. The temperature dependence of τ_α can be described by the Vogel–Fulcher–Tammann (VFT) equation [10]

$$\tau_\alpha(T) = \tau_\alpha^\infty \exp[B/(T-T_0)]$$

(2)

where τ_α^∞, T_0 (the Vogel temperature), and B are constants. The best-fit parameters were $\log(\tau_\alpha^\infty[s]) = -12.2 \pm 0.8$, $T_0 = 286 \pm 4$ K and $B = 1700 \pm 280$ K. From the common definition of the glass transition $\tau_\alpha(T_g) = 100$ s, $T_g \cong 338$K.
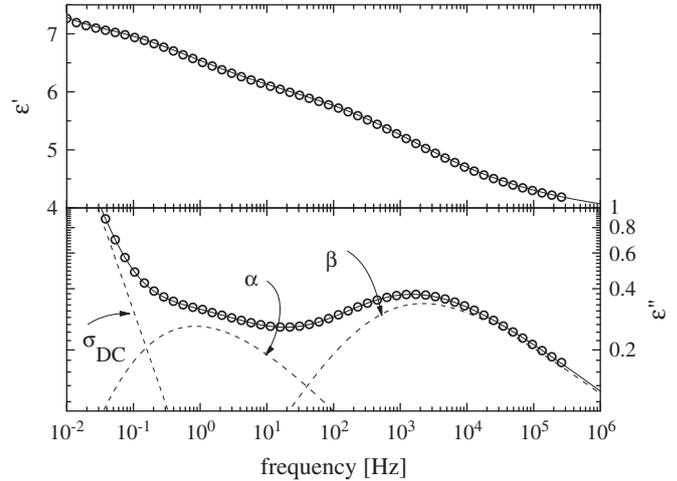
Fig. 2. Dielectric constant (top) and loss (bottom) of PMMA at 351.5 K. The solid lines are the fit of Eq. (1), with the dotted curves representing the respective contributions of the DC conductivity and the α and β relaxations.

The behavior of τ_β below the glass transition is described by the Arrhenius equation

$$\tau_\beta = \tau_\beta^\infty \exp(E_a/RT)$$

(3)

where R is the gas constant, τ_β^∞ the high temperature limit of τ_β, and E_a an activation energy. In the vicinity of T_g, E_a for the β process changes, with the obtained fit-parameters: $\log(\tau_\beta^\infty[s]) = -15.61 \pm 0.03$ and $E_a = 78.5 \pm 0.2$ kJ/mol at low temperature and $\log(\tau_\beta^\infty[s]) = -20.12 \pm 0.07$ and $E_a = 107.5 \pm 0.5$ kJ/mol at high temperature. This change in the behavior of the β process is also evident in its dielectric loss (Fig. 4). In the same figure the strong decrease of $\Delta\varepsilon_\alpha$ with increasing T is also shown. Similar behavior has been observed for high molecular weight PMMA, [11,12] as well as other materials [13]. σ_{DC} decreases with decreasing temperature, roughly inversely with the change in τ_α. However, since translational and rotational motions tend to decouple in the vicinity of T_g, generally $\sigma_{DC} \propto \overline{\tau}_\alpha^p$ with $p < 1$, behavior ascribed either to dynamic heterogeneity [14] or inherent differences in the cooperativity of the two dynamic processes [15] For this low molecular weight PMMA, we find $p = 0.52 \pm 0.01$ (inset to Fig. 3).
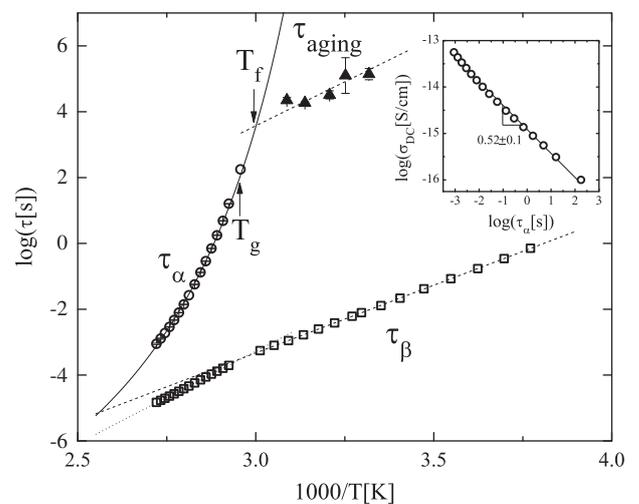
Fig. 3. Arrhenius plot of τ_α, τ_β, and τ_{aging}, the latter from fitting Eq. (4). The inset shows a double logarithmic plot of the conductivity versus the α relaxation time, yielding the indicated value of p.
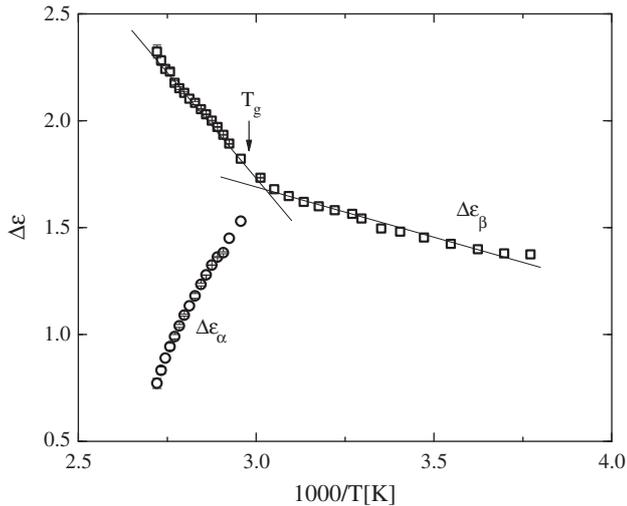
Fig. 4. Dielectric strength of the α and β processes versus inverse temperature. The different slopes of $\Delta\varepsilon_\beta$ characterize the equilibrium and glassy state.

Dielectric spectra are shown in Fig. 5 for aging at $T = 324.0$ K, a temperature at which any direct contribution from the α process is negligible at these frequencies. The β-spectra show a progressive decrease of amplitude, without any apparent change in the frequency of the peak maximum. As done previously for PB [4], we analyzed the evolution of the dielectric loss at a constant frequency, $\varepsilon''(f^*, t)$, using a stretched exponential function [16,17]

$$\varepsilon''(f^*, t) = C + D \exp\left[-\left(t/\tau_{aging}\right)^{\beta_{aging}}\right] \qquad (4)$$

where C, D, and β_{aging} are constants, and τ_{aging} is the aging time. As in the earlier study of PB [4], we fixed β_{aging} to the value of β_{KWW} determined for the α-peak above T_g (in this case, $\beta_{aging} = \beta_{KWW} = 0.38$), which limits the number of adjustable parameters to three. Omitted from the analysis are data during thermal equilibration ($t < 4$ h). The frequency f^* is arbitrary and has a negligible effect on the results [4].

The evolution of the dielectric loss at $f^* = 113$ Hz during aging at $T = 324.0$ K is displayed in Fig. 6. The solid line through the data is the fit of Eq. (4). To show visually that the behavior is well-described by a

stretched exponential, the linear variation of $\varepsilon''(f^*, t) - C$ versus $t^{\beta_{aging}}$ is shown in the inset.

The τ_{aging} determined using this procedure is included in the plot in Fig. 3 of the directly measured τ_α and τ_β. The behavior is very similar to that of PB [4], with τ_{aging} a continuation of τ_α into the glassy state. The relaxation times are smaller than the values extrapolated from the VFT behavior above T_g, in agreement with other observations [18–20].

Hodge [21] proposed an equation for the temperature behavior of the α process in the glassy state

$$\tau_\alpha(T) = \tau_\alpha^\infty \exp\left[B/T\left(1 - T_0/T_f\right)\right] \qquad (5)$$

where τ_α^∞, T_0 and B are the parameters from the VFT equation Eq. (2), and T_f is the fictive temperature. T_f is defined as the (hypothetical) temperature at which a property measured in a non-equilibrium state would be the equilibrium property. Deeply in the glassy state T_f becomes constant, so that Eq. (5) reduces to an Arrhenius equation. From the fit of Eq. (5) to τ_{aging} (only adjustable parameter is T_f), $T_f = 334 \pm 0.6$ K. Note that $\tau_\alpha(T_f) \sim 4000$ s.

Fig. 6. Evolution during dielectric loss at $f^* = 113$ Hz during aging at the indicated temperature. The solid line is the fit of Eq. (4) with constant $\beta_{aging} = 0.38$. The inset shows the same data after subtracting the fitting parameter C, plotted versus $t^{\beta_{aging}}$, with the line representing a linear fit.

Fig. 5. Dielectric β loss peak of PMMA during aging at 324.0 K. The aging times were from 2.6×10^4 to 8.4×10^5 s (top to bottom). The inset shows the corresponding changes in the dielectric strength of the β peak during aging; the line is a stretched exponential with $\beta_{KWW} = 0.38$ and $\tau_{aging} = 2.2 \times 10^4$ s.

Fig. 7. Power law slopes on the high and low frequency sides of the β dispersion as a function of aging time. The inset shows the (essentially constant) value of τ_β.

The change of $\Delta\varepsilon_\beta$ and τ_β with aging time are shown in insets to Figs. 5 and 7, respectively. The aging behavior of $\Delta\varepsilon_\beta$ can be described by Eq. (4) with $\beta_{aging} = 0.38$ and τ_{aging} determined from the change in ε'' at $f^* = 113$ Hz (Fig. 6). The frequency of the β peak maximum (i.e., $(2\pi\tau_\beta)^{-1}$) remains constant. However, there is an interesting change in the shape of the β peak during aging. Fig. 7 shows the time dependence of the exponents m and n describing the respective power law behaviors at low and high frequencies, $\varepsilon''(f) \sim f^m (f \ll f_{max})$ and $\varepsilon''(f) \sim f^{-n} (f \ll f_{max})$. These were calculated from the shape parameters in Eq. (1), as $m_\beta = a$ and $n_\beta = ab$. During aging m_β increases and n_β decreases; thus, the β peak becomes narrower at low frequency and broadens at high frequency. Consequently, although the peak maximum frequency (and thus τ_β) is essentially unchanged, the average relaxation time becomes shorter during aging. This differs from the finding of the prior study [4], in which the secondary relaxation time of PB shifted to higher frequency. However, the β peak for PB also became narrower at low and high frequencies with aging, which would make any shift in τ_β more evident.

4. Concluding remarks

The intense β process ($\Delta\varepsilon_\beta > \Delta\varepsilon_\alpha$) characteristic of PMMA facilitates utilizing its behavior during physical aging to follow structural relaxation in the glassy state, where τ_α are too long for direct measurement. Both $\Delta\varepsilon_\beta$ and τ_β change their T-dependences at temperatures for which $\tau_\alpha > 10^2$ s, indicative of a change in the behavior of the α relaxation. Previous modeling and NMR experiments interpreted the β relaxation in PMMA as "π-flips around the C–C bond to the backbone coupled with restricted rocking fluctuations of the backbone along its local extended chain axis" [5]. This means that reorientation of the side group is constrained by the backbone, so that changes in motion of the latter directly affect the intensity and time scale of the β process. Defining a crossover temperature, T_c, at which the extrapolated low and high temperature behaviors of the β process

intersect, we find $T_c = 338 \pm 5$ K from τ_β and $T_c = 330 \pm 6$ K from $\Delta\varepsilon_\beta$. These T_c bracket the value of T_f determined from fitting τ_{aging}, corroborating our determination of the temperature at which τ_α changes behavior (note that similar cooling rates were used for the two sets of measurements). The weaker effect of temperature in the glassy state is a consequence of the relative invariance of the structure to T; thus, changes effected by temperature are limited to thermal effects.

Acknowledgments

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