Journal of Non-Crystalline Solids 357 (2011) 282–285

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Aging of a low molecular weight poly(methyl methacrylate)

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ARTICLE INFO

Article history:
Received 5 April 2010
Received in revised form 30 June 2010
Available online 26 August 2010

Keywords:
Dielectric relaxation;
Glass transition;
Poly(methylmethacrylate)

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.

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.

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0022-3093/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2010.07.048

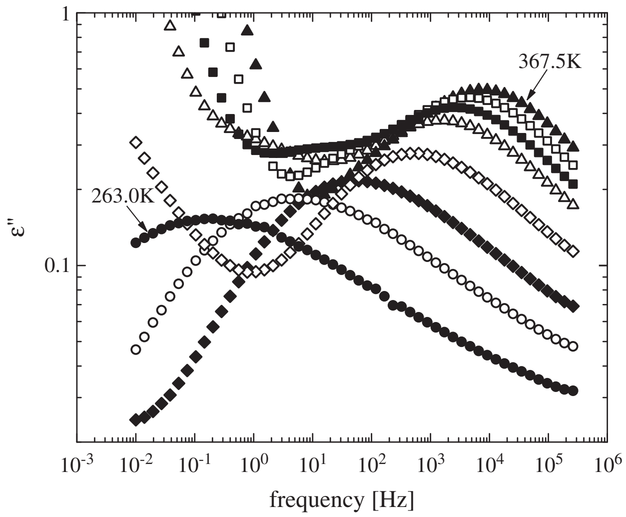

Fig. 1. Dielectric loss spectra for PMMA; from left to right the temperatures are 263.0, 290.5, 312.6, 338.2, 351.5, 357.4, 362.6, and 367.5 K. At higher T a strong σ_{DC} conductivity is evident.

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

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

$$\text{with} \quad \varphi_\alpha(t,\tau_\alpha) = \exp\left[-(t/\tau_\alpha)^{\beta_{KWW}}\right] \tag{1}$$

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 ($0<a$, $b\leq 1$), β_{KWW} the stretch parameter of the α process ($0<\beta_{KWW}\leq 1$), σ_{DC} the DC conductivity, and s ($0<s\leq 1$) 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 $0.94\leq s\leq 0.96$, 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]

$$\tau_\alpha(T) = \tau_\alpha^\infty \exp\left[B/(T-T_0)\right] \tag{2}$$

where τ_α^∞, T_0 (the Vogel temperature), and B are constants. The best-fit parameters were $\log(\tau_\alpha^\infty[s]) = -12.2\pm0.8$, $T_0 = 286\pm4$ K and $B = 1700\pm280$ K. From the common definition of the glass transition $\tau_\alpha(T_g) = 100$ s, $T_g \cong 338$K.

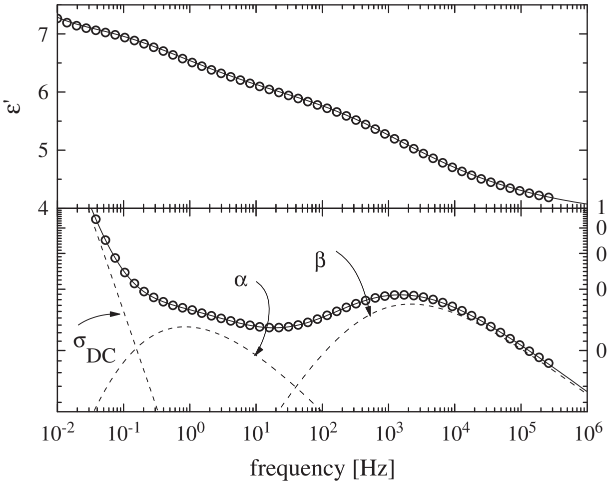

Fig. 2. Dielectric constant (top) and loss (bottom) of PMMA at 351.5 K. The solid lines are the fit of Eq. (1), with the dotted curves representing the respective contributions of the DC conductivity and the α and β relaxations.

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

$$\tau_\beta = \tau_\beta^\infty \exp\left(E_a/RT\right) \tag{3}$$

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: $\log(\tau_\beta^\infty[s]) = -15.61\pm0.03$ and $E_a = 78.5\pm0.2$ kJ/mol at low temperature and $\log(\tau_\beta^\infty[s]) = -20.12\pm0.07$ and $E_a = 107.5\pm0.5$ 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 $\sigma_{DC} \propto \tau_\alpha^{-p}$ 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 $p = 0.52\pm0.01$ (inset to Fig. 3).

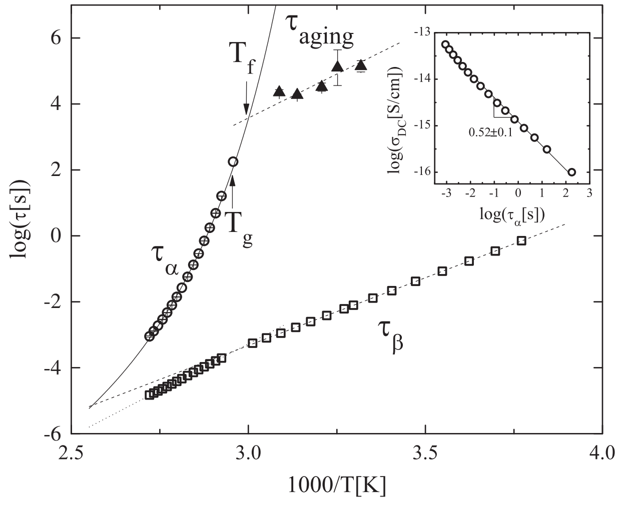

Fig. 3. Arrhenius plot of τ_α, τ_β, and τ_{aging}, the latter from fitting Eq. (4). The inset shows a double logarithmic plot of the conductivity versus the α relaxation time, yielding the indicated value of p.