# Temperature Dependence of the Johari−Goldstein Relaxation in Poly(methyl methacrylate) and Poly(thiomethyl methacrylate)

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ABSTRACT: To analyze the Johari−Goldstein (JG) secondary process, dielectric relaxation measurements were carried out on poly(methyl methacrylate) (PMMA) and poly(thiomethyl methacrylate) (PTMA). The latter has a sulfur atom replacing the oxygen in the ester of PMMA, making the pendant group much less polar. This weakens the intensity of the secondary relaxation, enabling facile resolution of the JG and primary structural relaxation peaks. We find that the JG relaxation time of PTMA has a substantially larger activation energy (factor of 2) in the liquid compared to the glassy state. Although deconvolution of the peaks in PMMA is more ambiguous due to the large dielectric strength of its JG relaxation, applying the same analysis leads to a very similar result. In light of previous results, we conclude very generally from their temperature-dependence that JG secondary motions sense the glass transition, consistent with their role as precursor to structural relaxation.
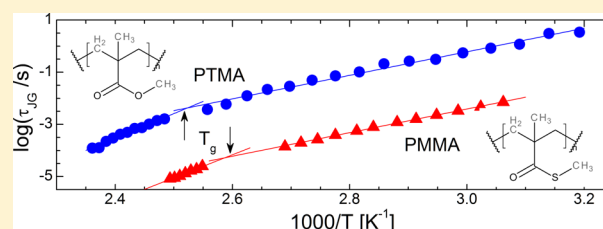
INTRODUCTION

Secondary relaxations are commonly observed in the dielectric spectra of materials.[1,2] For polymers these can arise from motion of pendant groups or other moieties involving intramolecular degrees of freedom. Secondary dynamics occur in the glassy state, and usually have no relation to structural relaxation and the glass transition.[3−5] The Johari−Goldstein (JG) process is different. Present in all liquids and polymers, even rigid molecules,[6,7] this process is the slowest secondary relaxation, and there is a large body of experimental data indicating that the JG relaxation functions as the precursor to structural relaxation (the α process).[8,9] Properties of the JG relaxation indicating a connection to the glass transition include: (i) pressure and temperature dependences of the JG relaxation time τ_{JG} that correlate with the breadth of the α-dispersion; (ii) the relationship between the separation of τ_{JG} and the primary relaxation time τ_α to properties of the α process; (iii) the change of temperature dependence of the JG dielectric strength across the glass transition temperature; (iv) merging of the JG and α relaxations at temperatures above T_g. Another property, the emphasis of the current work, is a change in temperature dependence of τ_{JG} at T_g.

In light of these properties, it can be seen that study of the JG relaxation can yield information about structural relaxation even in the glassy state, where the α-dynamics have largely ceased.[10−12] Of particular interest is the narrow range of thermodynamic conditions over which the JG and α processes can be measured simultaneously. This requires the relaxations to be separated in frequency and to have comparable intensities. Usually both relaxations can be measured only over frequencies where the two processes merge (or split), which is not far from the glass transition temperature, T_g. However, nearer T_g there is significant overlap of the dispersions, so that determination of the relaxation times τ_{JG}

and τ_α requires deconvolution of the peaks. Two methods to do this have been used: (i) If the processes are statistically independent, the peaks are additive in the frequency domain[13,14] and the dielectric loss is

$$\varepsilon''(\omega) = \Delta\varepsilon_\alpha \varepsilon_\alpha''(\omega) + \Delta\varepsilon_{JG} \varepsilon_{JG}''(\omega) \tag{1}$$

Equation 1 assumes the α and JG processes are uncoupled, but this is not obviously the case if the local environment is structurally relaxing while the dipoles undergo the JG relaxation.[15,16] (ii) Contemporaneous JG and α processes can be modeled by a relaxation function that in the time domain has the form[17]

$$\varepsilon(t) = f_\alpha \varepsilon_\alpha(t) + (1 - f_\alpha)\varepsilon_\alpha(t)\varepsilon_{JG}(t) \tag{2}$$

where f_α is the α-relaxation strength, and ε_α and ε_{JG} are the permittivities for the respective α- and JG processes. This leads to an apparent τ_{JG} that is dependent on properties of the α relaxation.[16]

How overlapping α and JG peaks are separated is significant because it can yield different results for the properties near T_g, a region critical to understanding the role of the secondary relaxation on the glass transition dynamics. One question is whether the temperature-dependence of τ_{JG} in the glass changes on heating through T_g, but the answer seems to depend on the method used to deconvolute the two peaks. Some workers report a substantial increase in the JG activation energy,[14,18−21] while others find there is no change in $\tau_{JG}(T)$ near T_g.[16,22] One way to circumvent the deconvolution problem is to separate the peaks by imposing conditions that affect the frequency of the

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processes differently. Some success along these lines has been obtained using high pressure,[9,23] physical aging,[24-26] and the addition of an antiplasticizing diluent.[27-29] The α relaxation is more sensitive than the JG process to the imposed changes, yielding greater separation in frequency of the peaks. These types of experiments have led to the conclusion that there is a change in the T-sensitivity of τ_{JG} near T_g.

Our interest herein is the dynamic behavior of polymethyl methacrylate (PMMA) near T_g. Multidimensional NMR experiments on PMMA reveal that the secondary relaxation involves 180° flips of the pendant carboxyl group; however, these are coupled to restricted rocking motion of the chain backbone in order to avoid steric interference from other segments.[30,31] The amplitude of this rocking motion increases with temperature, eventually becoming the conformational transitions of the backbone that underlie the segmental dynamics and T_g. Thus, the secondary relaxation in PMMA detected mainly as a side-group motion involves all atoms of the repeat unit, whereby it is designated a JG process. The high frequency side of the α dispersion in the dielectric spectrum of PMMA is very broad, causing its incursion on the intense JG peak. Assuming additivity of the α and JG relaxations in analyzing dielectric relaxation spectra for PMMA, Garwe et al.[14] observed a change in temperature dependence of τ_{JG} near T_g, which is consistent with the mechanism identified by NMR. However, from similar dielectric data but analyzed using eq 2, Bergman and co-workers[16,22] reached the opposite conclusion, that there is no change in $\tau_{JG}(T)$ near T_g. This ambiguous situation arises because there is no consensus on the correct method of deconvoluting overlapping α and JG peaks.

We address the issue by chemical modification of the PMMA, replacing the $-OCH_3$ moiety in the pendant ester with a $-SCH_3$ group. This changes the frequency of the segmental dynamics (T_g increases by 12 degrees), and also reduces the intensity of the β-process. The α and JG secondary peaks of the poly(thiomethyl methacrylate) (PTMA) can be accurately resolved, enabling an unambiguous determination of their temperature dependences. We find that the activation energy for the JG relaxation is significantly higher above T_g than in the glassy state. This suggests that the similar change in T-dependence of τ_{JG} for PMMA near T_g is not an artifact of the method of deconvoluting the dielectric spectra. These results support the idea that the JG relaxation senses the thermodynamic changes occurring near T_g;[32-34] thus, it can serve as a probe of structural relaxation.

■ EXPERIMENTAL SECTION

The thiomethyl methacrylate monomer and polymer were prepared using a modification of the method of Tatsuda et al.[35] Briefly, the thiomethyl methacrylate monomer was synthesized by reacting a two phase mixture of 40.3 g of methacryloyl chloride in methylene chloride with 183 g of a 15% aqueous sodium thiomethoxide solution, added dropwise at 0 °C. Distillation yielded 31.24 g of the monomer. The poly(thiomethyl methacrylate) was prepared by bulk polymerization of 1.56 g of monomer with 10.3 mg of AIBN initiator and 7.3 mg of 1-undecanethiol at 60 °C for 90 h, followed by dissolution and reprecipitation to yield 1.56 g of PTMA. Details of the polymerization and structural characterization of this polymer will be described elsewhere.[36] The PMMA (Arkema, Inc.) was courtesy of E. Baer of Case Western Reserve. The PTMA had a weight average molecular weight equal to 86.1 kg/mol and calorimetric T_g = 124 °C; for the PMMA M_w = 132 kg/mol and T_g = 112 °C. The structure of the repeat units is shown in Figure 1; both polymers were atactic and thus completely amorphous.
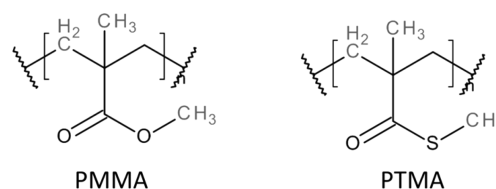

Figure 1. Chemical structures of the repeat units of the two polymers studied herein.

Dielectric spectra were measured using a Novocontrol alpha impedance analyzer. The sample cell consisted of parallel plates (diameter = 2 cm) with 0.1 mm Teflon spacers. During the measurements the sample was maintained in vacuo, using a custom closed-cycle helium cryostat (Cryo Ind.). Mechanical measurements employed an Anton Parr MCR 502 rheometer, using a parallel plate geometry (diameter = 8 mm), with frequencies in the range $10^{-3}-10^2$ rad/s. The sample was kept in a nitrogen atmosphere during the mechanical measurements.

■ RESULTS

Figure 2 compares the dielectric spectra of PTMA with that of PMMA at respective temperatures for which their τ_α are about
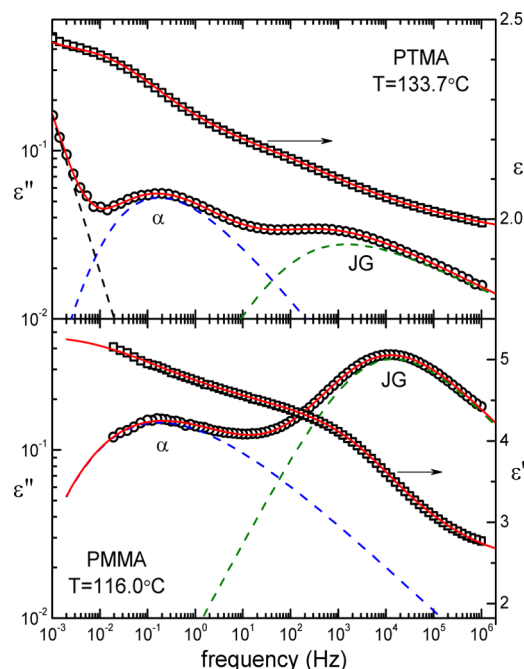

Figure 2. (Top) Real and imaginary dielectric permittivity of PTMA above the glass transition, showing resolved α and JG processes. (Bottom) Permittivity of PMMA above T_g, where the α process appears as a shoulder on the low frequency wing of the JG peak. In both figures the solid lines represent simultaneous fits of eq 3 to the data sets, with the individual contributions of both relaxations and the dc-conductivity indicated by dashed lines.

the same. The sulfur substitution mainly reduces the intensity of the JG process (by an order of magnitude), due to the weaker dipole on the side chain of PTMA; the electronegativity of S is about the same as that of carbon and much less than that of oxygen.[37] There is minimal difference in the dielectric strength of the α relaxation for the two polymers.

Both analysis methods (eqs 1 and 2) were applied to the PTMA data. The spectra were fit to a superposition of relaxation functions (eq 1), with the Kohlrausch–Williams–

Watts function used for the α peak and a Havriliak–Negami function for the JG relaxation[1]

$$\varepsilon^*(\omega) = \frac{\sigma_{DC}}{\varepsilon_0(i\omega)^n} + \varepsilon_\infty + \Delta\varepsilon_\alpha L_{i\omega}\left[-\frac{d\varphi_\alpha(t, \tau_\alpha)}{dt}\right]$$
$$+ \frac{\Delta\varepsilon_{JG}}{[1 + (i\omega\tau_{JG})^a]^b}$$
$$\text{with} \quad \varphi_\alpha(t, \tau_\alpha) = \exp[-(t/\tau_\alpha)^{\beta_{KWW}}] \tag{3}$$

$L_{i\omega}$ indicates the Laplace transform, ε_∞ is the high frequency permittivity, τ_i are the relaxation times, $\Delta\varepsilon_i$ the dielectric strengths, a and b the shape parameters for the JG relaxation, β_{KWW} is the KWW parameter for the α process, σ_{DC} the DC-conductivity, and n a constant less than or equal to one. Applying eq 2, the same forms were assumed for the individual relaxation functions, but the analysis was carried out in the time domain. Figure 3 shows that either method gives good fits to the experimental spectra.
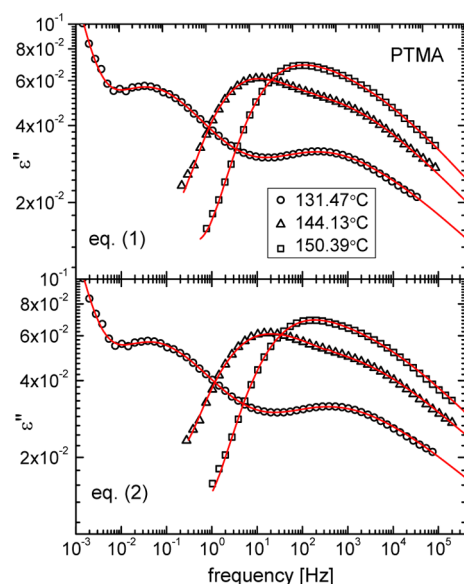
Figure 3. Dielectric loss of PTMA at three temperatures, analyzed assuming α and JG processes are (top) additive in the frequency domain or (bottom) contemporaneous and thus fit in the time domain using eq 2.

Figure 4 shows the temperature dependence of the relaxation times determined from the peak frequencies. Measurements of the α relaxation were limited at lower T by dc-conductivity. The $\tau_\alpha(T)$ above T_g is well described over several decades by the Vogel–Fulcher–Tammann (VFT) equation[1]

$$\tau_\alpha = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{4}$$

where τ_0 is the high T limiting value of the relaxation time, T_0 is the Vogel temperature, and B a constant. This equation predicts a divergence of τ_α below T_g; however, recent results reveal deviations from the VFT equation in the glassy state,[11,12,38−40] casting doubt on the existence of this divergence. Notwithstanding, the equation is adequate for the present data. For PTMA $\log(\tau_0) = -15.8 \pm 0.7$, $B = 2960 \pm 280$, and $T_0 = 325 \pm 4$; for PMMA $\log(\tau_0) = -10.9 \pm 1.9$, $T_0 = 337 \pm 15$, and $B =$
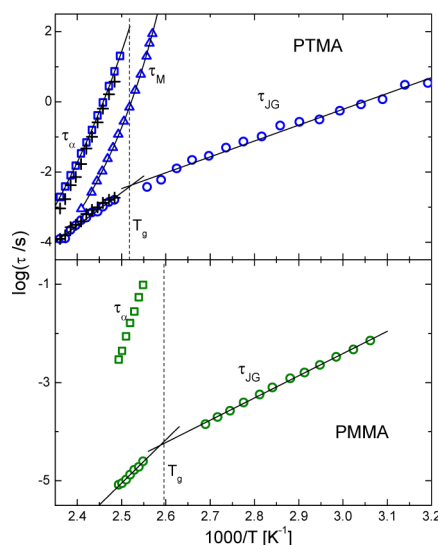
Figure 4. Arrhenius plots of the relaxation times for the two polymers. Lines are fits of the VFT equation (eq 4) to τ_α (squares) and τ_M (triangles), and of the Arrhenius equation (eq 5) to τ_{JG} (circles), the latter done separately for data above and below T_g. The relaxation times are calculated using eq 1, with values also included for PTMA above T_g obtained using eq 2 (crosses). No relaxation times are shown in the vicinity of T_g because only the high frequency side of the α peak is present in the spectra and there is a strong dc-conductivity contribution.

1280 ± 610. From these we calculate the fragility, $m = (d\log(\tau_\alpha))/(d(T_g/T))|_{T=T_g}$ at $\tau_\alpha(T_g) = 10$ s, obtaining 88 ± 13 for PTMA and 99 ± 15 for PMMA. The latter is less than a previously reported value for PMMA, which was based on $\tau_\alpha = 100$ s.[41,42] The apparent activation energy and fragility increase with increase τ_α (decreasing T_g).

Also included in Figure 4 are the local segmental relaxation times, τ_M, for PTMA, determined as the inverse of the frequency of the maximum in the mechanical loss modulus. The mechanical relaxation times have about the same temperature dependence as the dielectric τ_α, although as usual,[5,43,44] the τ_M are smaller than values from the dielectric loss. The best fit of the VFT equation to τ_M yields $\log(\tau_0) = -11.2 \pm 0.3$, $T_0 = 346.8 \pm 1.3$, and $B = 1284 \pm 65$. The fragility for $\tau_M = 10$ s is 105 ± 6, which agrees with the dielectric value within the experimental error.

The behavior of τ_{JG} in the glassy state is accurately described by the Arrhenius equation

$$\log(\tau_{JG}) = \log(\tau_{JG}^\infty) + \frac{E_{JG}}{RT} \tag{5}$$

where τ_{JG}^∞ is the high temperature limit of τ_{JG}, and E_{JG} is the activation energy. E_{JG} for the PTMA and PMMA are equivalent in the glassy state $(T < T_g)$, $= 84 \pm 2$ and 86 ± 2 kJmol^{-1}, respectively. The results are within 10% of the values from an empirical relationship proposed by Kudlik et al.,[45] $E_{JG} = 24RT_g$. However, these activation energies are 30% higher than predicted by ref 46 based on the coupling model. The τ_β^∞ differ by more than 2 orders of magnitude, $\log(\tau_{JG}^\infty) = -13.4 \pm 0.3$ for PTMA and -15.9 ± 0.3 for PMMA. Extrapolation of the τ_{JG} in Figure 4 above T_g would yield intersection with a value of τ_α about one hundred times smaller for PTMA than for PMMA. Thus, substitution of oxygen with sulfur results in a slower α relaxation, as well as a JG relaxation that is slower

relative to the α dynamics. Together with the observed decrease of the dielectric strength of the JG relaxation for PTMA, the behavior is consistent with the determination by Schmidt-Rohr[30,31] that the process involves flipping of the bulky pendant group, which requires rearrangement of the entire repeat unit. The sulfur atom is larger than oxygen, making the side group bulkier and its mobility more constrained. Results for a number of glass-forming materials have indicated that the time scale separating the JG and α processes at T_g varies inversely with the magnitude of the stretch exponent β_{KWW} for the α dispersion.[47] For PTMA $\beta_{KWW} = 0.38$ close to T_g, which is larger than the value of $\beta_{KWW} = 0.30$ for PMMA; this is consistent with the larger $\tau_{JG}(T_g)$ for PTMA.

Our main interest herein is the temperature dependence of the JG relaxation in the vicinity of T_g. For PTMA this is easily obtained from the fits to the permittivity spectra, since the JG peak is less dominant, so that either deconvolution method, eqs 1 or 2, gives the same τ_{JG}. As seen in Figure 4, there is a significant increase in the activation energy above T_g; $E_{JG} = 176 \pm 4$ kJ/mol, which is twice the value for the glassy state. Using the same analysis method, the behavior of PMMA is very similar, E_{JG} increasing above T_g to 172 ± 6 kJ/mol. In aging experiments on a lower molecular weight PMMA,[12] the temperature sensitivity of the α process decreased in the glassy state, exhibiting Arrhenius behavior below T_g. Thus, the smaller activation energy of the JG process below T_g mimics the change in temperature dependence of the α process. Finally we note that in accord with published results, the dielectric strength of the JG process changes at T_g (Figure 5). Such behavior, which mirrors the change in activation energy, has been reported for other glass-forming materials.[8]
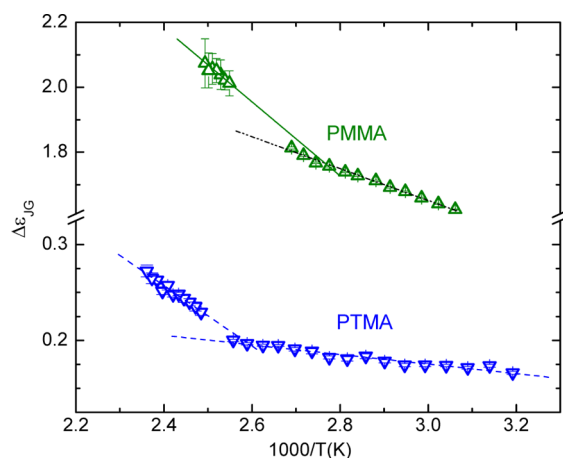

Figure 5. Dielectric strength of the JG process for PTMA and PMMA as a function of inverse temperature. A change in $\Delta\varepsilon_\beta$ occurs in the proximity of the glass transition. Solid lines are linear fits to the data above and below T_g.

■ SUMMARY

A chemical variation of the structure of PMMA reduces the dipole moment of the pendant group; consequently, the JG relaxation has lower dielectric strength and does not overwhelm the α relaxation. The uncertainty in deconvoluting the two peaks in PMMA is reduced for PTMA, enabling an unambiguous determination of the relaxation times for both the JG and α processes. The activation energy of τ_{JG} for PTMA increases 2-fold for temperatures above T_g compared to the

glassy state. Very similar behavior is found for PMMA, when the same statistical independence of the α and JG relaxations is assumed. We conclude that the two processes can be analyzed using eq 1, and moreover the conclusion drawn from earlier data analyzed in this manner[14,18−21] are correct: The activation energy of the JG relaxation changes at T_g. This means that the JG process senses the thermodynamic changes associated with the glass transition, consistent with its putative role as a precursor to structural relaxation.[1,2,7,8] Thus, the study of the JG secondary relaxation in glasses can yield insights into structural relaxation in glass-forming liquids.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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