

# Slow dynamics of the $\alpha$ and $\alpha'$ relaxation processes in poly(methyl methacrylate) through the glass transition studied by mechanical spectroscopy

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In this paper, low-frequency mechanical spectroscopy has been used to study poly(methyl methacrylate) (PMMA) melt around the glass transition temperature  $T_g$  for shedding light on its unique relaxation behaviors. The mechanical spectra show an asymmetrical broad structure with a maximum peak on the high-temperature side and a shoulder peak on the low-temperature side. The shoulder peak corresponds to the  $\alpha$  relaxation due to the local segmental motion; while the maximum peak is assigned to the  $\alpha'$  relaxation due to the slow motion of longer chain segments or chains. The  $\alpha$  relaxation mode has a stronger temperature dependence of relaxation time than the  $\alpha'$  mode, causing the  $\alpha'$  mode to merge with the  $\alpha$  mode with decreasing temperature toward  $T_g$ . Time-temperature superposition (TTS) breaks down in the entire temperature range due to the different friction coefficients of the  $\alpha$  and  $\alpha'$  relaxations. For only the  $\alpha'$  process, TTS is found to hold for PMMA melt, where the high-frequency decay of the mechanical loss decreases like a power law of the frequency with an exponent of  $-1/3$ . Moreover, compared with the dielectric results, the relaxation times of  $\beta$  and  $\alpha$  relaxations from mechanical measurements are about one order of magnitude slower than those from dielectric experiments. © 2009 American Institute of Physics.

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## I. INTRODUCTION

In past decades, the proper nature of molecular mobility in polymers near and above the glass transition has been a hot topic of controversy in the condensed matter physics. Poly(methyl methacrylate) (PMMA), probably the most fragile glass-forming polymer, exhibits many distinct relaxation behaviors, and its molecular dynamics has received much attention.<sup>1-5</sup> Two different relaxation processes in PMMA have been observed, the  $\alpha$  relaxation due to the translational movement of molecular chains and the  $\beta$  relaxation caused by the flipping movement of the whole ester side group.<sup>6-8</sup> The relaxation time of  $\alpha$  relaxation follows a Vogel-Fulcher-Tamman (VFT) law, while the  $\beta$  relaxation is described by an Arrhenius model.<sup>6,9</sup> These very different temperature dependences often lead to the fact that the relaxation times of the two processes become comparable at high temperature/frequency. This range is usually referred to as the “merging region.” The dynamics of PMMA in the merging region has been investigated by dielectric spectroscopy,<sup>6,9,10</sup> and the result shows that the dynamics can be described by the extrapolations from the low temperatures of the separate  $\alpha$  and  $\beta$  relaxations provided Williams' ansatz is used, where the nonexponential dielectric responses of the  $\alpha$  and  $\beta$  relaxations are described by the Havriliak-Negami (HN) function in the frequency domain. In addition, a much slower process, the  $\alpha'$  relaxation, was observed in PMMA above the glass transition temperature  $T_g$ .<sup>2,3,11,12</sup> The  $\alpha'$  relaxation, designed

as the liquid-liquid transition at the transition temperature  $T_{ll} \sim 1.2T_g$  by Boyer, was looked as a transformation from one liquid state to another one and arose from the collapse of localized short-range order or the onset of motion of entire polymer chains.<sup>13</sup> On the other hand, Plazek *et al.*<sup>14-16</sup> thought that the  $\alpha'$  relaxation was contributed from chain modes within the softening dispersion, composed of the sub-Rouse modes and the Rouse modes. The Rouse modes dominate the viscoelastic response in the glass-rubber transition region and contain in the order of 50 or more backbone bonds. The sub-Rouse modes are intermediate in character between the local segmental relaxation and the Rouse modes, involving on the order of ten backbone bonds. Although great efforts have been made to illuminate the dynamics close to  $T_g$ , the relaxation behaviors of PMMA from the glassy state to the liquid state are far from being understood.

Internal friction or anelastic relaxation forms the core of the mechanical spectroscopy method, widely used in solid-state physics and material science to study crystal structures, defects, and phase transitions in solids and liquids.<sup>17-22</sup> In particular, anelastic spectroscopy gives direct information about the molecular relaxation dynamics of materials.<sup>23,24</sup> Recently, it has proven to be valid and sensitive for probing the relaxation dynamics in soft matter such as biological matter and polymers on a large temperature range and frequency scale.<sup>25-28</sup> The  $\beta$  process of PMMA below  $T_g$  has been studied via mechanical spectroscopy;<sup>29</sup> however, detailed studies of the mechanical relaxation dynamics on PMMA far above and around  $T_g$  are more scarce. The aim of

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this work is to understand the mechanical relaxation processes in PMMA from the glassy state to the liquid state in more detail.

## II. EXPERIMENTAL

Methyl methacrylate (MMA) (Aldrich, 99% pure) was washed with 5% sodium hydroxide (NaOH) aqueous solutions and distilled water for three times, subsequently dried with anhydrous sodium sulfate, and then distilled in vacuum. It was stored in a refrigerator before use. The PMMA was synthesized by free radical polymerization in benzene at 343 K for 12 h, initiated by 0.04 mol/l 2,2'-azobisisobutyronitrile (AIBN). After the designated time, the product was precipitated in methanol and dried under vacuum at 313 K until the weight became constant. Weight-average molecular weight ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) of PMMA are  $3.4 \times 10^4$  g/mol and 1.5, respectively. Prior to the mechanical spectroscopy measurements, samples were kept at 410 K in vacuum for at least 24 h to remove the moisture content. The differential scanning calorimetry (DSC) showed a glass transition at 390 K.

The mechanical spectroscopy measurements were conducted on a developed low-frequency inverted torsion pendulum using the forced-vibration method. The apparatus consists of the traditional torsion shaft equipped with two coaxial cylindrical cells for liquid samples. The details of the device can be found elsewhere.<sup>30</sup> In the measurements, the inner cylinder is forced into torsional vibration by a time-dependent force  $F(t) = F_0 \sin(\omega t)$ . The angular displacement function of the cylinder,  $A(t)$ , is measured optically. In the case here, the response of the argument can be expressed as  $A(t) = A_0 \sin(\omega t - \phi)$ , where  $\phi$  is the phase difference between  $F(t)$  and  $A(t)$ . The mechanical loss of the oscillating system, characterized by  $Q^{-1}$ , is given by

$$Q^{-1} = \frac{1}{2\pi} \frac{\Delta W}{W} = \frac{1}{2\pi} \frac{\oint F dA}{\int_0^{\pi/2} dW - \frac{1}{4} \Delta W} = \frac{1}{2\pi} \frac{F_0 A_0 \pi \sin \phi}{\frac{1}{2} F_0 A_0 \cos \phi} = \tan \phi, \quad (1)$$

where  $\Delta W$  and  $W$  are the dissipated energy and the maximum stored energy per cycle, respectively.

In the measurement, the mechanical loss ( $\tan \phi$ ) and the relative modulus ( $G = F_0/A_0$ ) were measured over a frequency range of  $5 \times 10^{-3}$  to 90 Hz for each of the temperatures at which the PMMA sample was isothermally kept. In our experiments, isothermal measurements were first carried out at low temperatures, and thereafter the isothermal spectra were measured at predetermined temperature intervals by increasing the sample's temperature in steps.  $G$  and  $\tan \phi$  of the sample were also measured over a temperature range of 360–530 K at fixed frequencies of 0.05, 0.5, and 8.0 Hz. In all tests, the samples were protected by argon with a pressure of 0.1 MPa to avoid oxidation and degradation.

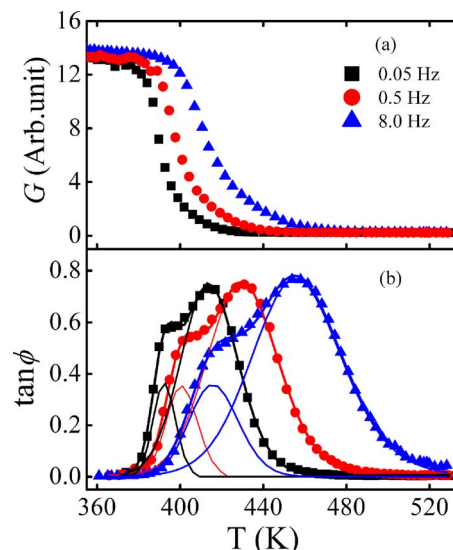


FIG. 1. (Color online) Temperature-dependent relative modulus (a) and mechanical loss (b) of PMMA at 0.05, 0.5, and 8.0 Hz. The solid lines are the fitting of the  $\alpha$  and  $\alpha'$  peaks, respectively. Two peaks appear explicitly.

## III. RESULTS AND DISCUSSION

The complex mechanical spectra ( $\tan \phi$  and  $G$ ) of PMMA are shown in Figs. 1(a) and 1(b) at three frequencies in the temperature range of 360–530 K. The mechanical loss peak shows an asymmetrical broad structure with a shoulder at the low-temperature side. This peak could be well fitted by two peaks (labeled as  $\alpha$  and  $\alpha'$  peaks) with distribution in relaxation time using a nonlinear fitting method,<sup>31</sup> as shown in Fig. 1(b). The  $\alpha$  and  $\alpha'$  peaks are both thermally activated relaxation processes, as they shift toward higher temperature with increasing frequency. For simplicity, we describe the processes as the  $\alpha$  relaxation and  $\alpha'$  relaxation, respectively. Note that the  $\alpha'$  relaxation exhibits a stronger frequency dependence than the  $\alpha$  relaxation. For example, as the frequency varies from 0.5 to 0.05 Hz, the  $\alpha$  peak shifts from about 401 to 392 K with an interval of 9 K, which is close to the common shift interval of 7 K of  $T_g$  (Ref. 23) when the frequency increases/decreases a decade times; whereas the  $\alpha'$  peak shifts from 430 to 413 K with a larger interval of 17 K. Therefore, the  $\alpha'$  peak moves faster to lower temperature than the shoulder peak with decreasing frequency. As a result, the whole loss peak becomes narrower and narrower, and the  $\alpha$  peak is almost superposed by the  $\alpha'$  peak at low frequencies due to the merging of the  $\alpha'$  peak with the  $\alpha$  peak. A similar phenomenon has also been observed in chlorinated butyl rubber (CIIR).<sup>32</sup> The fact means that the peak positions of the  $\alpha'$  peaks are more sensitive to frequency. In reverse way, the relaxation time of the  $\alpha$  mode is more sensitive to temperature than that of the  $\alpha'$  mode. As longer mobile units are more sensitive to the frequency, the longer chain segments of the slow process have more backbone bonds than the local segments of the  $\alpha$  process.<sup>32</sup>

Since the minimum temperature of the  $\alpha$  peak agrees approximately with the glass transition temperature determined by DSC measurement, the  $\alpha$  peak is associated with the glass transition and is known to be ascribed to the cooperative rearrangement of chain segments when  $T_g$  is

approached.<sup>33</sup> The local segmental motion usually involves correlated local motion of only a few backbone bonds. On the other hand, the  $\alpha'$  peak should be attributed to the motion of longer chain segments or chains because they are expected to move at a higher temperature.<sup>32</sup> The  $\alpha'$  relaxation was usually considered as the liquid-liquid transition in the previous dielectric measurement.<sup>12</sup> The liquid-liquid transition is a very weak third-order transition having both relaxational and thermodynamic characters, much as the glass transition does, and is looked as a transformation from one liquid state to another one.<sup>13,34</sup> However, the occurrence of liquid-liquid transition was discredited by Plazek and Orbon.<sup>14</sup> They presented that the loss peak at constant frequency as a function of temperature could not be used as an evidence for any kind of thermodynamic transition above  $T_g$ , and DSC measurements on a number of different purified amorphous polymers failed to yield any reproducible evidence for liquid-liquid transition. The  $\alpha'$  mode is contributed from chain modes within the softening dispersion, composed of the sub-Rouse modes and the Rouse modes.<sup>14-16</sup> There is no liquid-liquid transition, and the only change is the variation of the intermolecular coupling causing a smooth change-over of the liquid from one dynamic regime to the other at the crossover temperature  $T_c \sim 1.2T_g$ .<sup>35-38</sup> Therefore, there exist many similarities between the ideas of liquid-liquid transition and the observed dynamic crossover. The differences between them are that the crossover is purely dynamic in origin and no thermodynamic transition is evidenced.<sup>38,39</sup> Herein the  $\alpha'$  mode was proven to be a dynamic relaxation process. In view of the criticism made by Plazek for the use of the word "transition," it is more appropriate to call the  $\alpha'$  mode as the liquid-liquid transformation.<sup>37</sup> It is suggested that rotational motion might contribute stronger to segmental dynamics, while translational motion might contribute more to chain dynamics.<sup>40</sup> This might explain stronger temperature variation of the  $\alpha$  mode than the  $\alpha'$  mode since the rotational motion has a stronger temperature variation than the translational motion.

To get a better insight of relaxation dynamics of PMMA above  $T_g$ , the frequency-domain mechanical spectra of PMMA in the temperature range of 413–457 K are measured, as shown in Figs. 2(a) and 2(b). It should be noticed that below 428 K, two relaxation modes can be discriminated in the measuring frequency region; while they cannot be separated above 428 K since the peak frequency of the relaxation mode in the high-frequency side herein may be comparable to the inherent frequency of the pendulum, which is about 250 Hz at room temperature and decreases with increasing temperature. In the lined-shape analysis of the spectra below 428 K by the method of least square, we used a simple addition of two HN functions for fitting the  $\alpha$  and  $\alpha'$  peaks relying on the additive ansatz.<sup>41</sup> The relaxation function used includes broadness and skewness of the relaxation time distributions,

$$\tan \phi = \frac{\Delta}{[1 + (i\omega\tau)^\lambda]^\gamma}, \quad (2)$$

where  $\Delta$  is the relaxation strength and  $\lambda$  and  $\gamma$  determine the profiles of relaxation spectrum,  $0 < \lambda \leq 1$ ,  $0 < \gamma \leq 1$  ( $\lambda = \gamma$

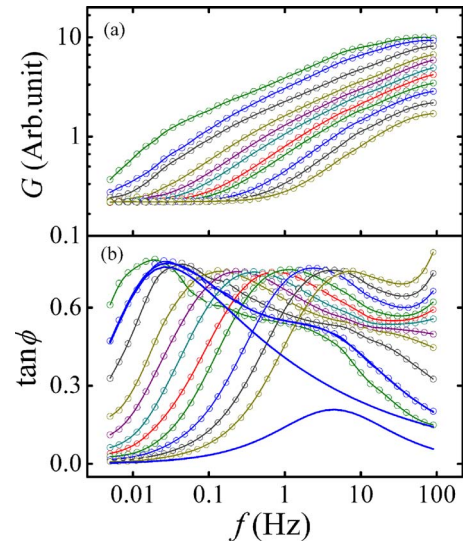


FIG. 2. (Color online) Frequency dependence of relative modulus (a) and mechanical loss (b) of PMMA at the temperatures of 413, 418, 423, 428, 432, 437, 441, 445, 449, 453, and 457 K (from left to right). Solid curves are HN best fits to the mechanical loss data at 418 K.

$=1$  corresponds to the standard Debye relaxation). The stretching parameter  $\beta_{KWW}$  is approximately equal to  $(\lambda\gamma)^{1/1.23}$ . The details of the fitting results are given only at 418 K for clarity, as shown in Fig. 2. The stretching parameters  $\beta_{KWW}$  for the  $\alpha$  and  $\alpha'$  peaks at 418 K are 0.72 and 0.32, respectively.

Time-temperature superposition (TTS) is the basic principle widely used for analysis of dynamics in supercooled liquids and polymers, expressing the fact that the shape of the response function remains the same when the system is cooled.<sup>40,42,43</sup> When TTS applies, the response is only shifting its characteristic time and amplitude if the liquid is cooled. Here we analyze the frequency-dependent mechanical loss to investigate whether TTS is obeyed. In Fig. 3, a normalized master curve of the loss data for PMMA above  $T_g$  is plotted. This plot shows that the shape of the relaxation process varies with lowering  $T$ , indicating that TTS breaks down in the entire temperature range. The failure of TTS is clearly related to the presence of the  $\alpha$  peak. This fact reflects different friction coefficients of the  $\alpha$  and  $\alpha'$  relaxations.<sup>40,43</sup> The decoupling of chain and segmental dy-

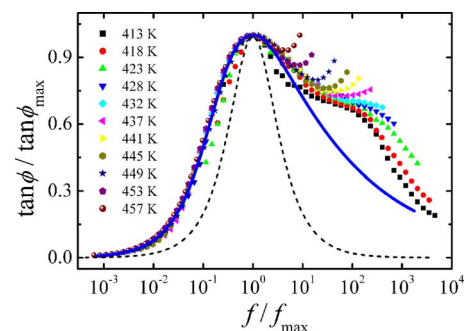


FIG. 3. (Color online) Normalized master curves of PMMA above  $T_g$ . The pure exponential (Debye) relaxation is shown with the dashed line. The fitting to the data of the  $\alpha'$  peaks in terms of HN equation is shown with a solid line. A subpeak of  $\alpha$  process is visible in the high-frequency flank below 428 K.



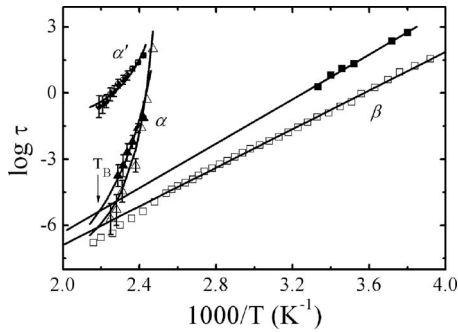


FIG. 4. Temperature variations of relaxation time  $\tau_{\text{HN}}$  of PMMA extracted with HN model for mechanical  $\alpha$  (▲) and  $\alpha'$  (●) relaxations, dielectric  $\beta$  (□) and  $\alpha$  (△) relaxations (Ref. 6), and mechanical  $\beta$  (■) relaxation (Ref. 29). Data of the  $\beta$  relaxation are fitted by Arrhenius model, while data of the  $\alpha$  and  $\alpha'$  relaxations are fitted in terms of VFT equation.

namics occurs in the melt. Without signature of  $\alpha$  relaxation TTS of  $\alpha'$  process is found to hold for PMMA melt where the high-frequency decay of the mechanical loss decreases like a power law of the frequency with an exponent of  $-1/3$  (solid lines in Fig. 3). It is known that the high-frequency decay of the dielectric loss of  $\alpha$  process is characterized by a power-law behavior with an exponent of  $-1/2$ .<sup>42,44</sup> This difference may originate from different friction coefficients of the  $\alpha$  and  $\alpha'$  relaxations and needs more effort.

The temperature dependence of mean relaxation time  $\tau$  of PMMA could be obtained by fitting the peak with distribution in relaxation time by Eq. (2). As is well known, the temperature dependence of viscoelastic properties near and above  $T_g$  is usually described by the VFT equation,

$$\tau(T) = \tau_0 \exp[B/k_B(T - T_0)], \quad (3)$$

where  $\tau_0$  is the pre-exponential factor,  $T_0$  is the critical temperature (or “Vogel temperature”), and  $B$  is a pseudoactivation energy. Figure 4 displays the temperature dependences of mean relaxation time  $\tau$  of PMMA for mechanical  $\alpha$  and  $\alpha'$  relaxations. For comparison, the relaxation time of  $\beta$  and  $\alpha$  relaxation processes for PMMA from dielectric spectroscopy<sup>6</sup> over the same temperature and the relaxation time of  $\beta$  relaxation from mechanical spectroscopy<sup>29</sup> at the low temperature are also shown in Fig. 4. It can be also seen that relaxation time of the  $\alpha$  relaxation has a stronger temperature dependence than the  $\alpha'$  relaxation. In addition, the relaxation time associated with  $\beta$  relaxation is largely distributed and obeys an Arrhenius law  $\tau = \tau_0 \exp(\Delta H/k_B T)$ , while those associated with the  $\alpha$  and  $\alpha'$  process are nearly narrowly distributed and better fitted by a VFT law. The values of fitting parameters for the  $\beta$ ,  $\alpha$ , and  $\alpha'$  relaxations are shown in Table I.

The temperature dependences of  $\beta$  and  $\alpha$  relaxations obtained in mechanical and dielectric experiments are similar since they differ only by constant factors. Vertically shifting the relaxation times from dielectric spectroscopy shows that on one hand our mechanical spectroscopy results reproduce the temperature dependence of the relaxation time of PMMA well, but that on the other hand our relaxation times are about one order of magnitude slower than those from dielectric experiments. The temperature at the merging point,  $T_B$ , of  $\alpha$  and  $\beta$  relaxations is obtained by the extrapolation of the

TABLE I. Fitting parameters of the relaxation time associated with the  $\beta$ ,  $\alpha$ , and  $\alpha'$  relaxation modes from mechanical and dielectric measurements.

Relaxation modes	Parameters	Mechanical results	Dielectric results
$\beta$	$\tau_0$ (s)	$2.96 \times 10^{-17}$	$3.65 \times 10^{-17}$
	$\Delta H$ (eV)	0.99	0.82
$\alpha$	$\tau_0$ (s)	$1.34 \times 10^{-11}$	$1.48 \times 10^{-11}$
	$B$ (eV)	0.11	0.10
	$T_0$ (K)	365	371
$\alpha'$	$\tau_0$ (s)	$3.46 \times 10^{-3}$	
	$B$ (eV)	0.034	
	$T_0$ (K)	376	

$\beta$  relaxation from low temperatures. Note that  $T_B$ ,  $\sim 453$  K, from the mechanical measurement is consistent with that from the dielectric data. However, the characteristic relaxation time  $\tau(T_B)$  at this point is  $\sim 10^{-5.5}$  s, higher than that of  $\sim 10^{-6.5}$  s from dielectric spectroscopy. This may be the consequence of the different relaxing species excited by mechanical torsional strain and electric field couple.<sup>7</sup> The ratio of  $T_B/T_g$  ( $=1.16$ ) agrees approximately with the value of  $T_c/T_g$  by experiments<sup>35-38</sup> and mode-coupling theory.<sup>45</sup>  $\tau(T_B)$  is very similar to the value of  $\tau(T_c)$  noticed for many small molecular and polymeric liquids and called “magic” relaxation time.<sup>46</sup>  $\tau(T_c)$  was found to be independent of pressure. The merging of  $\alpha$  and  $\beta$  processes was suggested to be related to some critical relaxation time at which dynamics of glass-forming liquids crosses over from a liquidlike behavior to a solidlike behavior on a molecular scale.<sup>39,46</sup>

#### IV. CONCLUSION

In conclusion, we have investigated the slow relaxation dynamics of  $\alpha$  and  $\alpha'$  relaxations of PMMA near and above  $T_g$  using mechanical spectroscopy. The relaxation time of the  $\alpha$  relaxation has a stronger temperature dependence than the  $\alpha'$  relaxation. TTS breaks down in the entire temperature range due to the different friction coefficients of the  $\alpha$  and  $\alpha'$  relaxations. Combined with the results of mechanical  $\beta$  relaxation and dielectric  $\beta$  and  $\alpha$  relaxations, the temperature dependences of  $\beta$  and  $\alpha$  relaxations obtained in mechanical and dielectric experiments are similar since they differ only by constant factors. The merging point is about 453 K for both the experiments, but the relaxation time at the merging point from mechanical data is  $\sim 10^{-5.5}$  s, higher than  $\sim 10^{-6.5}$  s from dielectric data.

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