

Effects of molecular weight on the liquid-liquid transition in polystyrene melts studied by low-frequency anelastic spectroscopy

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A substantial internal friction peak associated with the liquid-liquid transition (T_{ll}) has been observed in polystyrene (PS) melts with different molecular weights M_w . The peak is of the relaxation type and suggested to be caused by the cooperative rearrangement of PS chains. The relaxation time follows the Vogel-Fulcher-Tamman equation. With increasing M_w , the PS melt exhibits a higher energy barrier, a smaller concentration of mobile species, and a stronger coupling between mobile species at T_{ll} . In addition, to quantify the strength of the temperature dependence of the relaxation time, a parameter m_{ll} is defined for PS melt according to Angell's fragility concept. The value of m_{ll} decreases with increasing M_w , indicating a slower cooperative rearrangement of PS chains toward T_{ll} . Moreover, at $M_w \leq 52.5$ kg/mol, m_{ll} rapidly drops with M_w , while it more slowly decreases at $M_w > 52.5$ kg/mol. The fact suggests more topological constraints due to the intrachain interactions in very long chains. © 2008 American Institute of Physics. [DOI: 10.1063/1.2904588]

I. INTRODUCTION

The most significant transition in amorphous polymers is the glass transition (T_g), a change from glass to viscoelastic melt. Aside from T_g , there is another transition called the liquid-liquid transition (T_{ll}), generally located at $(1.1-1.3)T_g$.¹ Recently, growing attention has been paid to T_{ll} due to the damping capability of polymers.^{2,3} Since Boyer⁴ proposed the existence of T_{ll} in polystyrene (PS) in 1966, it has been the subject of a large amount of studies. Many experimental methods were exploited to prove the existence of T_{ll} and understand its nature, including torsional braid analysis, viscosimetry, differential scanning calorimetry, dynamic mechanical analysis, spectroscopic methods, nuclear magnetic resonance, thermally stimulated current, and so on.²⁻¹⁸ Generally, T_{ll} is viewed as the transition of the polymer melts from the "immobile liquid" to the "true liquid."^{1,7,14,15} The nature of the transition was used to be attributed to the breakage of short-range intermolecular interaction and the onset of motion of melts,¹² the change in the state of localized order,^{7,10,14} the slippage of chain entanglements and chain ends,¹¹ and the dissociation of chain clustering.^{17,18} Although a great deal of research has been done on T_{ll} , little information has been reported so far with regard to influence of molecular weight (M_w) on the dynamics near and above T_{ll} , where the variation of M_w is directly related to the change of interchain or intrachain interaction in polymer melts.

Anelastic spectroscopy (internal friction technique) has been widely used in solid-state physics and materials science to study crystal structures, defects, and phase transitions in solids,¹⁹⁻²² as well as dynamics in liquids and polymers.²³⁻²⁵ In particular, anelastic spectroscopy gives direct information about the molecular relaxation dynamics in materials.^{26,27}

Recently, on the basis of anelastic spectra data, it has been confirmed that there exists a liquid-liquid transition in amorphous PS melts.^{17,18,28} In this letter, we have investigated T_{ll} of PS melts with different molecular weights by low-frequency anelastic spectroscopy. The aim of the present study is to detect how change of molecular weight affects the dynamics of PS melt near and above T_{ll} .

II. EXPERIMENTAL

Monodisperse PS (M_w from 10.2 to 215 kg/mol) was prepared by anionic polymerization. The weight-average molecular weights and molecular weight distributions are listed in Table I.

The anelastic spectroscopy measurements were conducted on a developed low-frequency inverted torsion pendulum by using the forced-vibration method. The details of the device can be found elsewhere.²⁹ According to this technique, the internal friction (Q^{-1}) was calculated by measuring the loss angle (ϕ) between applied stress and resulting strain. Meanwhile, the dynamic modulus (G) was calculated from the ratio between the stress and strain. The measurements were carried out with a torsion strain amplitude of 3×10^{-5} and a temperature-cooling rate of 0.33 K/min. For

TABLE I. Characteristics of PS with different molecular weights. The value of T_p , Q_{\max}^{-1} , and β are extracted from the fitting of Fig. 5 measured at a vibration frequency of 3 Hz.

M_w (kg/mol)	M_w/M_n	T_p (K)	Q_{\max}^{-1} (± 0.005)	β (± 0.05)
10.2	1.04	405	1.23	2.58
15.6	1.11	414	1.20	2.63
27.9	1.02	432	1.18	2.90
52.5	1.05	456	1.04	3.79
122	1.03	462	0.87	3.92
215	1.05	506	0.87	4.16

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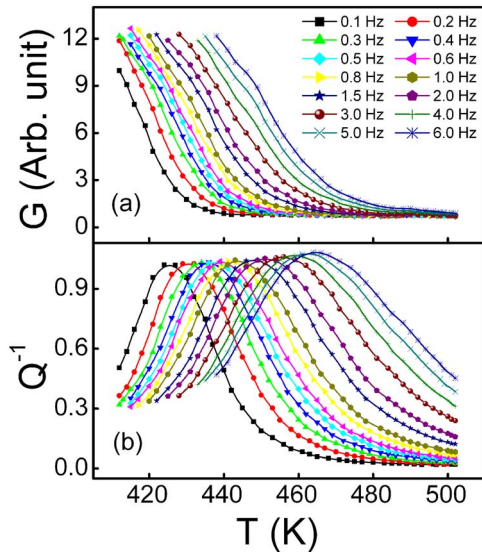


FIG. 1. (Color online) The curves of (a) dynamic modulus and (b) internal friction vs temperature for PS melt with $M_w=52.5$ kg/mol at various frequencies.

given torsion frequencies (f), the internal friction and dynamic modulus of the samples were measured as a function of temperature. The sample was protected by argon with a pressure of 0.1 MPa to avoid oxidation and degradation.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) present the anelastic spectroscopy (dynamic modulus G and internal friction Q^{-1}) of one example of PS melt with $M_w=52.5$ kg/mol at various frequencies. An obvious internal friction peak was observed at about 430–470 K, accompanied by a corresponding decrease on the dynamic modulus. Note that the peak is thermally activated, as it shifts to higher temperatures with increasing vibration frequency. So there exists a thermally induced anelastic relaxation process instead of phase transition. As described in the previous work,¹⁸ the internal friction peak here was associated with T_{II} of PS. As the temperature surpasses T_g , only a part of interaction between chains breaks and some segment entanglements still remain in the liquid (“fixed liquid”), which finally leads to the T_{II} where all these interactions disappear and a pure liquid state (true liquid) is reached.^{7,14} For a thermally relaxation process, we have the Arrhenius relation of $\tau = \tau_0 \exp(E/kT)$, where τ is the relaxation time, τ_0 is the relaxation time extrapolated to infinite temperature, and E is the activation energy. The internal friction peak occurs at the following condition:

$$\omega\tau = 1, \quad (1)$$

where ω is the circular frequency ($=2\pi f$). So at the peak, it gives

$$\ln \tau = -\ln \omega = \ln \tau_0 + E/kT_p, \quad (2)$$

where T_p is the temperature at the peak. Through the $\ln \tau$ vs $1/T_p$ curve (as shown in Fig. 2), we obtained $E=1.75$ eV and $\tau_0=10^{-20\pm 1}$ s for PS melt with $M_w=52.5$ kg/mol. Here, τ_0 is so low compared to the general values which are higher than $10^{-16\pm 1}$ s,¹⁹ strongly indicating that it is a cooperative relax-

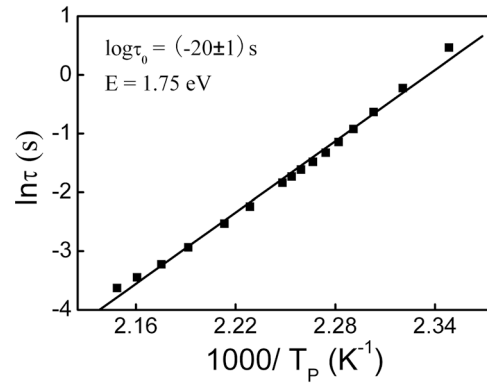


FIG. 2. (Color online) Logarithmic relaxation time $\ln \tau$ vs reciprocal of net peak temperature $1/T_p$ for PS melt with $M_w=52.5$ kg/mol.

ation process.²⁸ For the relaxation near and above T_g , the relaxation time τ follows the Vogel–Fulcher–Tamman (VFT) equation,

$$\tau = \tau_0 \exp \left[\frac{E'}{k(T - T_0)} \right], \quad (3)$$

where T_0 is the critical temperature (or “Vogel temperature”), and E' is termed as an “activation energy,” physically representing an Arrhenius-like temperature activation energy. Analogically, combined with Eq. (1), we have

$$\ln \tau = -\ln \omega = \ln \tau_0 + E'/k(T_p - T_0). \quad (4)$$

At many given T_0 , through the $\ln \tau$ vs $1/k(T_p - T_0)$ curve, we obtained different $\ln \tau_0$ and E' by the linear fitting procedure. The final values of $\ln \tau_0$ and E' are obtained when the root mean square error [standard deviation (SD)] between the linear fitting curve and the actual data reaches the minimum at one given T_0 (as shown in Fig. 3). The values of τ_0 , E' , and T_0 of PS melts with different molecular weights M_w are plotted in Figs. 4(a)–4(c), respectively. From Fig. 4, we can see that the activation energy parameter E' decreases from 0.230 to 0.070 eV and T_0 increases by 80 K when M_w is increased from 10.2 to 215 kg/mol. [Note by inspection of Eq. (3) that *decreasing* E' corresponds to *increasing* temperature sensitivity.] Thus, the higher temperature sensitivity for the relaxation time with M_w is found.³⁰

Figure 5 shows the variation of internal friction versus temperature for PS melts with different molecular weights at a vibration frequency of 3 Hz. With increasing M_w , the dissipation peak shifts to higher temperature and becomes lower

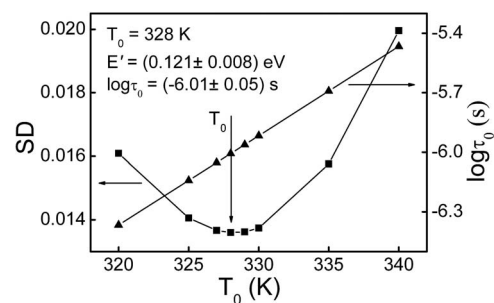


FIG. 3. The variations of the root mean square error (SD, ■) and the logarithmic relaxation time ($\log \tau_0$, ▲) at various temperatures T_0 .

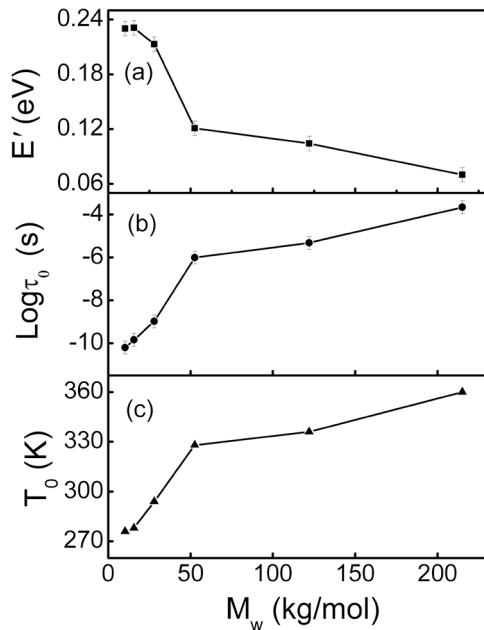


FIG. 4. (Color online) (a) Activation energy E' , (b) pre-exponential factor of relaxation time τ_0 , and (c) critical temperature T_0 vs molecular weight M_w .

and broader. The resulting peak temperature T_p , the peak height Q_{\max}^{-1} , and the distribution parameter β of peak width are obtained by a fitting procedure³¹ used in Refs. 32 and 33. The values of them are also shown in Table I. Note that T_p increases with increasing M_w , and Q_{\max}^{-1} decreases. The increasing T_p indicates a higher energy barrier at the transition,³⁰ and the decreasing Q_{\max}^{-1} implies a smaller concentration of mobile species.³⁴ It should also be noted that β is an increasing function of M_w (Table I), indicating a broader distribution of mobile species involved in the movement. The dissipation peak occurs when the vibration frequency is close to the intrinsic frequency originating from the mobility of the polymer chain between topological knots.¹⁷ The increasing distribution of mobile species with M_w causes a larger distribution of the intrinsic frequency of mobile species. As a result, the boarder dissipation peak with M_w is observed under thermal energy.

On the other hand, the increasing β may imply a stronger coupling between mobile species in the relaxation

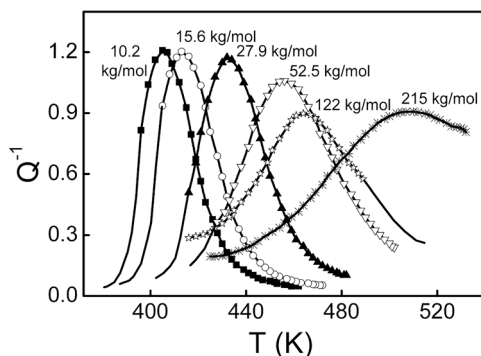


FIG. 5. (Color online) The variation of internal friction vs temperature for PS melts with different molecular weights obtained at a vibration frequency of 3 Hz.

process.³⁵ The coupling parameter n ($0 \leq n < 1$), which is closely related to the topological constraints of the entangled system, increases as the coupling strength increases.^{30,36} As discussed in Refs. 32 and 35, a higher value of β generally corresponds to a bigger coupling parameter n . Thus, the larger the M_w of PS is, the more topological constraints and the stronger coupling between PS chains would be.

To further study the effect of molecular weight on the dynamics and quantitatively measure the dynamics of T_{\parallel} itself, a parameter of polymer melt m_{\parallel} is proposed. As we know, the dynamic fragility m is widely used and defined as³⁷

$$m = \left. \frac{d \log \tau}{d(T_{\text{ref}}/T)} \right|_{T=T_{\text{ref}}}, \quad (5)$$

where T_{ref} is a reference temperature. Replacing f with $1/(2\pi\tau)$ and taking the first derivative of the VFT expression, one obtains

$$m = \frac{E}{kT_{\text{ref}}(\ln 10) \left(1 - \frac{T_0}{T_{\text{ref}}}\right)^2}. \quad (6)$$

Equation (6) indicates that the fragility m is indeed the relative variation rate of the temperature dependence of relaxation time τ toward T_{ref} . Angell used T_g to normalize temperature because it is one of the most important characteristic temperatures associated with the glass transition. Likewise, the liquid-liquid transition temperature T_{\parallel} is a more important characteristic temperature related to the relaxation process for an entire polymer chain. If T_{\parallel} is used to normalize T , the parameter expressed in Eq. (6) can be rewritten as

$$\begin{aligned} m_{\parallel} &= \left. \frac{d \log \tau}{d\left(\frac{T_{\text{ref}}}{T}\right)} \right|_{T=T_{\text{ref}}} = \left. \frac{d \log \tau}{d\left(\frac{T_{\parallel}}{T}\right)} \right|_{T=T_{\parallel}} \\ &= \frac{E}{kT_{\parallel}(\ln 10) \left(1 - \frac{T_0}{T_{\parallel}}\right)^2}. \end{aligned} \quad (7)$$

Here, m_{\parallel} is just a parameter to measure the relative variation rate of the temperature dependence of relaxation time τ toward T_{\parallel} . “Strong” melts exhibit lower m_{\parallel} values at T_{\parallel} , and “fragile” melts exhibit higher values at T_{\parallel} . The T_{\parallel} -scaled Arrhenius plot for PS melts with different molecular weights is shown in Fig. 6(a), and the values of m_{\parallel} calculated from Eq. (7) are shown in Fig. 6(b). The increasing steeper trends of $\ln \tau (T_{\parallel}/T)$ with decreasing M_w [Fig. 6(a)] indicate the more fragile melts.

The value of m_{\parallel} decreases with increasing M_w [Fig. 6(b)], implying that the PS melt experiences a slower chain rearrangement toward T_{\parallel} . This behavior is comprehensible because the dissociation of chain clustering of one PS chain would be hindered by the increasing steric hindrances of surrounding PS chains. Moreover, we can observe from Fig. 6(b) that m_{\parallel} rapidly decreases with the molecular weight at $M_w \leq 52.5$ kg/mol. However, it more slowly decreases at $M_w > 52.5$ kg/mol. The M_w dependence of m_{\parallel} suggests the

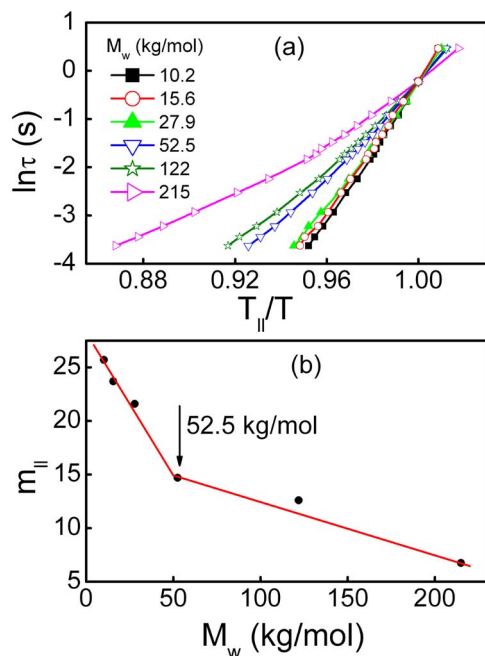


FIG. 6. (Color online) (a) T_{II} -scaled Arrhenius plot for PS melts with different molecular weights and (b) the M_w dependence of the parameter m_{II} of PS melts; the solid line is a guide for the eyes.

different topological constraints caused by interchain or intrachain interactions at $M_w \leq 52.5$ and $M_w > 52.5$ kg/mol. The interchain interactions are dominant in short chains. As the length of chains increases, the role of intrachain interactions becomes more significant and they might dominate interchain interactions in very long chains. Thus, the PS chains tend to slowly relax into the free space above 52.5 kg/mol.

IV. CONCLUSION

We present the anelastic spectra of a series of PS with different molecular weights M_w near and above T_{II} . The liquid-liquid transition is a relaxation process through the cooperative rearrangement of PS chains. The PS melt with a higher M_w shows a higher energy barrier, a smaller concentration of mobile species, and a stronger coupling between mobile species at T_{II} . Based on the established methods in supercooled liquid, a parameter m_{II} is defined to characterize the dynamics near and above T_{II} . It is found that m_{II} decreases with increasing M_w , indicating a slower cooperative rearrangement of PS chains toward T_{II} . In addition, at $M_w \leq 52.5$ kg/mol, m_{II} sharply decreases with increasing M_w , while it more slowly decreases at $M_w > 52.5$ kg/mol, implying more topological constraints due to the intrachain interactions. The parameter m_{II} is found to reflect well the topological characteristics of polymer melts near and above T_{II} .

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