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Liquid-to-liquid relaxation of polystyrene melts investigated by low-frequency anelastic spectroscopy

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Abstract

Polystyrene melts with a narrow distribution of molecular weights far above the glass transition have been investigated by use of low-frequency anelastic spectroscopy. A liquid-to-liquid relaxation occurs when the molecular weight (M_n) is either above or below the critical molecular weight (M_c) for chain entanglement. As the molecular weight increases, the relaxation temperature (T_p) increases and the movement of the polymer chain is easier for short chains than for long chains. In the range we investigated ($M_n \sim 1.0 \times 10^4 - 2.1 \times 10^5$), the relaxation time (τ_p) corresponding to the dissipation peak is related to the molecular weight by $\tau_p \propto M^{2.6}$. This is consistent with theoretical prediction. We suggest that the dissociation of the chain clustering is responsible for the liquid-to-liquid relaxation.

1. Introduction

The dynamics of polymer chains in melt is important for correlating polymer structure and processing. Theoretically, four dynamic modes have been predicted. They are reptation behavior, Rouse chain motion between two adjacent entanglement points, chain slippage through entanglement links and the primitive chain length fluctuation [1–9]. The crossover of the dynamics was also expected [10–12]. Experimentally, early studies have demonstrated segment motion and chain slippage in polystyrene [13] and polyisoprene melts [14]. Recent investigations have revealed the contour length fluctuations, the crossover from segment Rouse motion to local reptation, and the local conformational transitions through torsional motions in some polymer melts [15–17].

The liquid–liquid transition or relaxation in polystyrene melt at a temperature far above the glass transition temperature (T_g) was observed more than 30 years ago [18]. Such

Table 1. Characteristic data of polystyrene samples.

Sample	M_n	M_w/M_n	T_g (K)	τ_0	α_f
PS1	9 786	1.04	359	3.9×10^{-6}	1.6×10^{-3}
PS2	14 080	1.10	362	3.3×10^{-6}	1.4×10^{-3}
PS3	20 966	1.03	366	1.2×10^{-6}	1.1×10^{-3}
PS4	27 357	1.02	374	1.1×10^{-6}	1.0×10^{-3}
PS5	35 617	1.02	375	1.3×10^{-6}	9.9×10^{-4}
PS6	114 146	1.03	377	5.9×10^{-6}	9.0×10^{-4}
PS7	204 908	1.05	379	6.0×10^{-5}	9.0×10^{-4}

a phenomenon was further manifested in poly(methyl methacrylate) [19], styrene-*co*-ethyl acrylate random copolymer melts [20] and poly(*n*-alkyl methacrylates) [21–23]. Frenkel *et al* [24] proposed that it arises from segment–segment contacts in the same or neighboring chains. Some studies have also indicated that it is dynamic in origin [25–27]. However, the exact nature of the relaxation is not yet clear.

Low-frequency anelastic spectroscopy has been used for studying crystal structures, defects and the phase transitions of metals [28]. It has been verified to be valid and effective for liquid structures [29, 30]. In principle, it can measure any polymer melts which do not thermally degrade at the measurement temperature. The strain imposed on the sample, which varies sinusoidally with time, has an amplitude as small as $\sim 10^{-5}$ rad. Thus, the so-called Weissenberg rod-climbing effect and slip of polymer melt can be avoided, and the volume of the measured melts is invariant during the measurement. In addition, the precision of the set-up with multi-frequencies is as small as $\sim 10^{-4}$.

It is known that the molecular weight and its distribution strongly affect the dynamics of the polymer chains and the rheological properties of the polymer melts. Polydispersity usually masks the effect of molecular weight. In the present work, we have prepared a series of narrowly distributed polystyrene samples with molecular weights ranging from 1×10^4 to 2×10^5 g mol⁻¹ using anionic polymerization. By using low-frequency anelastic spectroscopy, we have investigated the molecular weight dependence of the dissipation ($\tan \Phi$). Our aim was to examine the dynamics of the polystyrene in melt.

2. Experimental section

2.1. Preparation and characterization of polystyrenes

The narrowly distributed polystyrene (PS) samples were prepared by anionic polymerization in tetrahydrofuran (THF) with *n*-butyllithium as the initiator at a temperature of ~ 78 °C under a pressure below 10^{-6} mm [31]. Gel permeation chromatography (GPC) on a Waters 1515 was used to determine the molecular weight and the molecular weight distribution (weight average molecular weight/number average molecular weight, M_w/M_n) of the samples with a series of monodisperse polystyrenes as the calibration standard and THF as the eluent with a flow rate of 1.0 ml min⁻¹. The temperature of glass transition (T_g) of each sample was measured on a Shimadzu differential scanning calorimeter (DSC) with a heating rate of 20 °C min⁻¹. T_g was taken as that centered at the point of transition. The characteristic data are summarized in table 1.

2.2. Energy dissipation measurements

The dissipation measurements were conducted on a developed torsion pendulum apparatus equipped with a vacuum pump and a gas shielding system. The sample was placed between

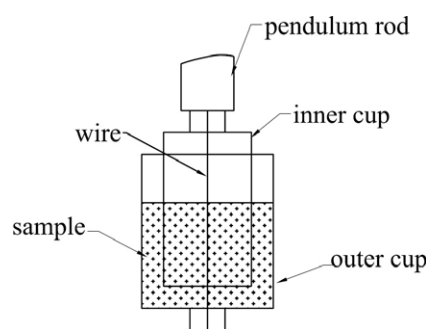


Figure 1. Schematic illustration of the low-frequency anelastic spectroscopy.

two bell-like cups in a stainless-steel vessel (figure 1). The inner cup immersed in the liquid sample, which was linked to a pendulum rod, was used as the sensor. Stress was applied to the sample by the inner cup. A magnetic bearing guiding device was constructed on the top of the pendulum rod to lessen the radical swing of the sensor. A computer automatically controlled all the experiments and the data collection. The details can be found elsewhere [29, 30]. The sample was subjected to a strain varying in a sinusoidal manner with time, which led to the stress varying in the same manner. All these processes were controlled by the computer.

For a completely elastic sample, the stress and strain are in-phase. For a viscoelastic sample, the viscous component would cause the stress and strain to be out of phase, i.e., there is a phase lag between them, which leads to the energy dissipation. The dynamic modulus is a relative value resulting from the value of I_{stress} (the amplitude of the stress) / I_{strain} (the amplitude of the strain) ratio. With given torsion frequency (f) and constant amplitude, the energy dissipation ($\tan \Phi$) of the polymer melt was measured as the function of temperature, where Φ is the phase angle at which the strain lags the stress.

The value of the energy dissipation was measured in this apparatus with a constant strain amplitude of 3×10^{-5} rad and sixteen torsion frequencies in the range of 0.1–6.0 Hz. The sample was degassed in a vacuum oven at 80 °C for 10 h to remove the adsorbed water before the measurement. Each measured sample weighed 3.0 g. The cooling rate was 0.33 °C min⁻¹. The sample was protected by argon with a pressure of 0.1 MPa to avoid oxidation and degradation.

3. Results and discussion

Figures 2 and 3 show the temperature dependence of energy dissipation ($\tan \Phi$) and dynamic modulus of PS melts at the measured frequencies 0.1 Hz, 1.0 Hz and 6.0 Hz, where $M_n = 20\,966$ and 114 146, respectively. It is known that the entanglement has an effect on the dynamics of a polymer. For PS, the critical molecular weight (M_c) for entanglement is about 3×10^4 – 4×10^4 g mol⁻¹ [13, 18]. Accordingly, entanglement is not expected in the former but in the latter. For PS melt either with or without entanglement, as temperature increases, $\tan \Phi$ exhibits a peak around a certain temperature (T_p). Correspondingly, the modulus decreases and becomes flat at temperatures above T_p . It is known that the temperature or structural change of polymer chains can lead to a change of intrinsic frequency, the intrinsic frequency originates from the mobility of the polymer chain between topology knots. On the other hand, when the measured frequency is close to the frequency originating from the mobility of the polymer chain between topology knots at a given stress, the relaxation exhibits an energy dissipation

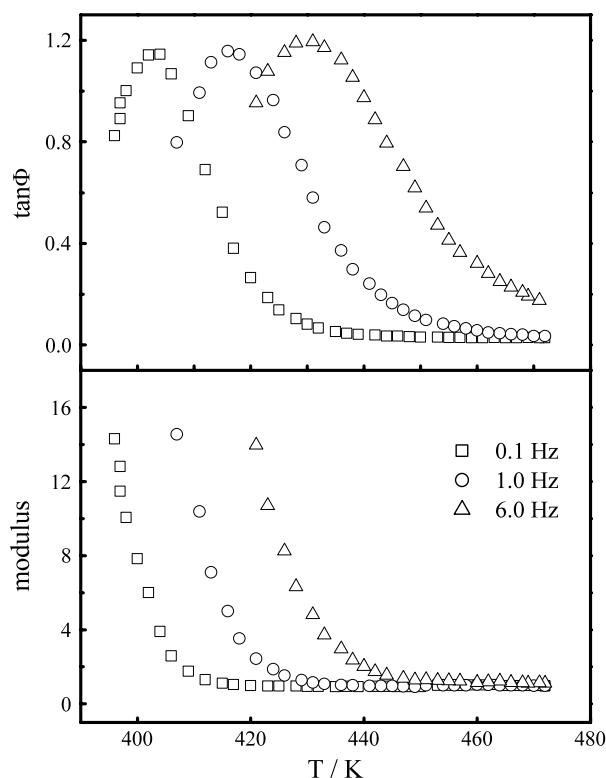


Figure 2. Temperature dependence of energy dissipation ($\tan \Phi$) and dynamic modulus of PS melts with $M_n = 20966$.

peak. Since the temperature T_p is far above T_g (table 1), the dissipation peak here should be attributed to the so-called liquid-to-liquid relaxation [18]. Figures 2 and 3 show that T_p shifts to a higher temperature as the measured frequency increases. The position of the peaks changes noticeably with measuring frequencies, which indicates the relaxation has a dynamic nature rather than that of a thermodynamic phase transition, where the corresponding peaks do not move with measured frequencies [32]. This is consistent with the theoretical [26, 27] and experimental results [33]. Figures 2 and 3 clearly show that the occurrence of the relaxation is independent of the entanglement. However, a higher molecular weight leads to a higher T_p at the same frequency. In other words, the relaxation of a longer chain needs a higher temperature to be activated.

Figures 4 and 5 show the circular frequency (ω) dependence of the dissipation ($\tan \Phi$) of PS melts at different temperatures with $M_n = 20966$ and 114 146, respectively, where $\omega = 2\pi f$ with f being the measured frequency. It can be seen that a dissipation peak at a higher temperature corresponds to a higher measured frequency. On the other hand, at the same measured frequency, a PS with a higher molecular weight exhibits a dissipation peak at a higher temperature. This is understandable, as initiating the motion of polymer chains is increasingly difficult as the length of the chain increases, and a higher temperature is required.

Figure 6 shows the molecular weight (M_n) dependence of T_p of PS melts, where the measuring frequencies are 0.5 and 2.0 Hz. Obviously, T_p increases rapidly with the molecular weight at $M_n \lesssim 3 \times 10^4 \text{ g mol}^{-1}$. However, T_p increases more slowly at $M_n \gtrsim 3 \times 10^4 \text{ g mol}^{-1}$.

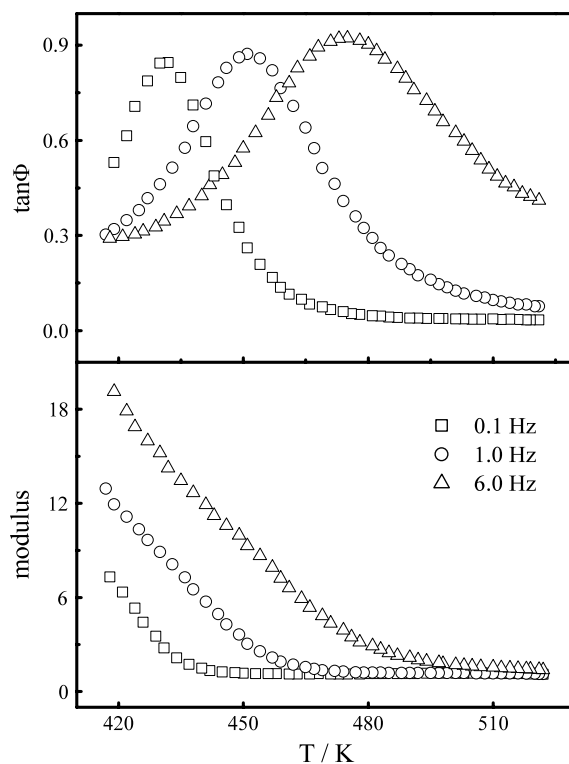


Figure 3. Temperature dependence of energy dissipation ($\tan \Phi$) and dynamic modulus of PS melts with $M_n = 114\,146$.

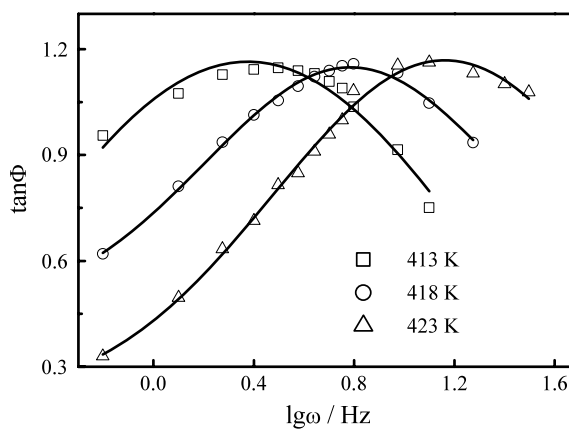


Figure 4. Circular frequency (ω) dependence of energy dissipation ($\tan \Phi$) of PS melts at different temperatures, where $M_n = 20966$.

It is clear that the critical molecular weight (M_c) is $\sim 3 \times 10^4 \text{ g mol}^{-1}$. The solid lines fit the data points very well and the functional form of the fit is:

$$y = y_0 + A_1(1 - e^{-x/t_1}) + (1 - e^{-x/t_2}) \tag{1}$$

where y_0 , A_1 , A_2 , t_1 and t_2 are all fitting parameters.

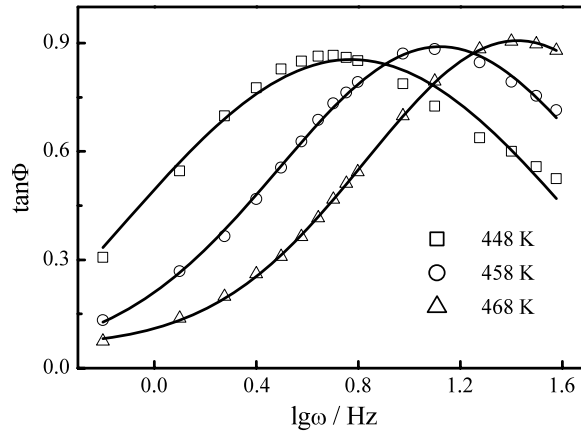


Figure 5. Circular frequency (ω) dependence of energy dissipation ($\tan \Phi$) of PS melts at different temperatures, where $M_n = 114\,146$.

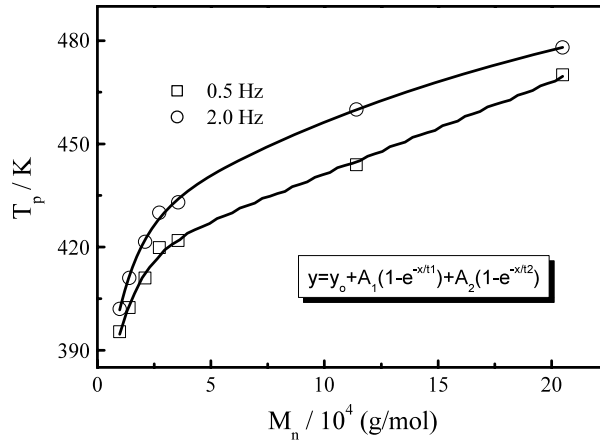


Figure 6. Molecular weight (M_n) dependence of dissipation peak temperature (T_p) of PS melts, where the measuring frequencies are 0.5 and 2.0 Hz.

Our results are in agreement with those previously reported [8]. It is known that the interchain and intrachain interactions are greatly dependent on the molecular weight; namely, the interchain interactions dominate the intrachain interactions in short chains. As the length of the chain increases, the role of the intrachain interactions becomes more important and it might dominate interchain interactions in very long chains. The M_n dependence of T_p shown in figure 6 suggests that the competition between interchain interactions and intrachain interactions at $M < M_c$ and $M > M_c$ is different.

Figure 7 shows the temperature dependence of the relaxation time (τ) of PS with different molecular weights. The dissipation peak occurs when $\omega\tau = 1$, where $\omega = 2\pi f$ and f is the measured frequency. We found the relaxation time (τ) can be described by Vogel–Fulcher–Tamman (VFT) equation [34–36]:

$$\tau = \tau_0 \exp[\alpha_f(T - T_\infty)]^{-1} \quad (2)$$

where τ_0 is the pre-exponential factor, α_f is the thermal expansion coefficient of the free volume, and T_∞ is the critical temperature at which any mobility is frozen. With $T_\infty = 341\text{ K}$ [37], the

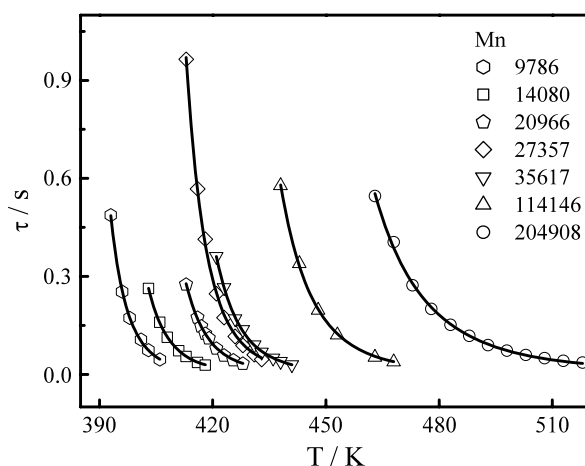


Figure 7. Temperature dependence of relaxation time (τ) of PS melts with different molecular weights, where the measuring frequency is 2.0 Hz.

fitting of relaxation time at each temperature yields the values of α_f and τ_0 for each PS sample (table 1). Thus, the result of equation (1) for each PS melt with a certain molecular weight can be obtained. Figure 7 shows that relaxation time decreases with temperature because the mobility of segments becomes rapid with the increase of temperature, which leads to rapid slippage of the whole chain at a higher temperature. On the other hand, as the molecular weight increases, the relaxation time becomes longer. This is understandable because a shorter chain with a smaller size is easier to pack into the available free space between chains via relaxation. Meanwhile, for a certain mass of PS melt, if the mass is made of shorter chains, the total number of the chain ends will be less than that of the mass made of longer chains, so that the former readily relax into the free volume associated with the chain ends. Particularly, when $M > M_c$, the relaxation also involves conformational change of the chains.

By using the VFT equation (equation (2)), relaxation time values of different PS melts at the same temperature can be obtained. Figure 8 shows the molecular weight (M_n) dependence of relaxation time (τ_p) corresponding to the dissipation peak with the reference temperature of 433 K used by Onogi *et al* [38] when they studied the rheological properties of monodisperse polystyrenes. Thus, the curve is represented by the power law $\tau_p \propto M^{2.6}$. Obviously, such a relation independent of molecular weight indicates the relaxations at either $M < M_c$ and $M > M_c$ have the same source. It has been predicted that $\tau \propto M^2$ for Rouse motion and $\tau \propto M^3$ for pure reptation motion [2], while numerous experiments give $\tau \propto M^{3.4}$ for the latter [39]. The relation $\tau_p \propto M^{2.6}$ clearly indicates that the relaxation is not due to the reptation motion or Rouse motion.

For polymer melts, the simulation by Kremer *et al* [40] reveals that the exponent (α) for the relation between the diffusion coefficient (D) and the molecular weight (M), i.e., $D \propto M^{-\alpha}$, is more than 2 due to the crossover effects that arise from the competition between leading correction terms originating from tube length fluctuation and higher-order terms [12]. Since $\tau \propto D^{-1}$, we have $\tau \propto M^\alpha$. Another simulation demonstrates $\alpha \sim 2.5 \pm 0.04$ [41]. Taking the memory effects due to material inhomogeneity (the extent of polymer chain entanglement in concentrated solutions of long polymer chains can be nonuniform where some regions of space are more ‘tangled up’ at a given time than others) and cooperative molecular motion, Douglas *et al* [42] predict $\alpha = 2.3$ – 2.5 . So far, the exponent has not been experimentally confirmed

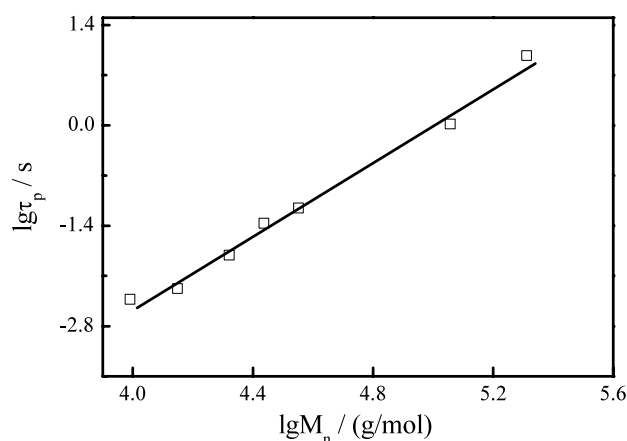


Figure 8. Molecular weight dependence of relaxation time (τ_p) of PS melts corresponding to the dissipation peak, where the reference temperature is 433 K.

in polymer melt. However, in entangled polystyrene solutions, the experimental investigations did show $D \propto M^{-\alpha}$ with $\alpha \sim 2.5$ [43]. The exponent ($\alpha \sim 2.6$) revealed in the present study suggests that the liquid-to-liquid relaxation in polymer melt should relate to the dissociation of the chain clusters (supramolecular structure) through the cooperation of the chains. Chain cluster is ubiquitous in polymer melts [44]. In PS melts above T_g , PS chains inevitably cluster or overlap with a number of free spaces or holes regardless of the chain length. Obviously, both the interchain interactions and intrachain interactions would result in chain clusters. As reported by Podesva [44], the clusters are dynamic structures; when the temperature is high enough (about T_p), the chains tend to relax into the free space and the supramolecular structure is destroyed, leading to the liquid-liquid relaxation.

4. Conclusions

In conclusion, the investigations on the liquid-to-liquid relaxation in melts of narrowly-distributed polystyrenes by use of the low-frequency anelastic spectroscopy lead to the following conclusions. Low-frequency anelastic spectroscopy is effective in studying relaxation in polymer melts. There indeed exists a liquid-to-liquid relaxation in polystyrene melts, the occurrence of which is independent of entanglement. Our experiments suggest that the relaxation arises from the dissociation of chain clustering.

Acknowledgments

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