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Local Segmental Dynamics of Low Molecular Weight Polystyrene: New Results and Interpretation

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ABSTRACT: The molecular dynamics of an 1100 low molecular weight polystyrene are reexamined by photon correlation spectroscopy measurements. The new experimental data combined with recoverable creep compliance data taken previously on the same sample provides information on the local segmental motion in a wide time window of more than 11 decades. Significant reduction of the "fragility" (i.e., a scaled temperature dependence of the retardation time) of the low molecular weight polystyrene compared with high molecular weight polystyrene, seen first by Santangelo and Roland by shear modulus measurement, is confirmed. The broader time window available in the present work shows for the first time that, unlike high molecular weight polystyrene, the dispersion of the low molecular weight sample is strongly temperature dependent and narrows with increasing temperature. By considering the low molecular weight polymer as a blend of chain ends and inner repeat units, the results are interpreted by the coupling model.

Introduction

The glass temperature, T_g, of most linear polymers is independent of molecular weight, M, as long as M is sufficiently larger than the critical molecular weight for entanglement, M_c.[1] However, if M falls below M_c and if hydrogen bonding is absent, a significant decrease of T_g with decreasing M is generally observed.[1−6] The decrease is well-described by the Fox−Flory equation

$$T_g = T_{g,\infty} - K/\bar{M}_n \tag{1}$$

where $\bar{M}_n$ is the number average molecular weight. The drop in T_g from the glass temperature for $\bar{M}_n = \infty$, $T_{g,\infty}$, is attributed to the increasing number density of chain ends present in polymers with lower molecular weight.[2−4] At temperatures above $T_{g,\infty}$, Fox and Flory found a linear increase in the specific volume v of polystyrenes with $1/\bar{M}_n$, which is interpreted as reflecting changes in the average density of packing with the concentration of end groups.[2,3] The idea that there is an excess free volume above the glass temperature due to the presence of chain ends was shown by Fox and Flory to be consistent with eq 1. This was further discussed in the work by Fox and Loshaek.[4] The increase in the number density of chain ends has generally been accepted to be the cause of the drop in T_g with a decrease in $\bar{M}_n$. However, how exactly the presence of chain ends changes all aspects of the molecular dynamics of the local segmental motion including the reduction in T_g, like the parent problem of glass "transition" itself,[7,8] is still an open question. From the wealth of experimental data on molecular dynamics of glass-forming materials obtained by conventional methods and microscopic probes such as quasielastic neutron scattering,[7,8] it can be concluded that the free volume concept may be correct to some extent but it alone cannot explain all the properties. The free volume concept seems unnecessary in situations where a glass transition has been observed at constant volume by a change of pressure. Nevertheless, neither can one conclude that the consideration of free volume is irrelevant. In fact, the free volume concept has been found to be consistent with many experimental data. We are not going to pass any judgment on the free volume concept here except to say that the concept alone cannot explain *all* aspects of molecular dynamics of glass transition. It is in this spirit that we reexamine the change of molecular dynamics of polystyrene with decreasing molecular weight by performing more experimental measurement using photon correlation spectroscopy. This task seems to be a timely and worthwhile undertaking in view of a recent work by Santangelo and Roland (SR)[9] in which dynamic mechanical relaxation measurements of local segmental motions in low and high molecular weight polystyrenes were presented and compared. The dispersion of the local segmental motions as measured by photon correlation spectroscopy, dielectric relaxation, dynamic mechanical relaxation, and creep compliance has been well-fitted[7] by either the Kohlrausch−Williams−Watts function,[10,11]

$$\phi(t) = \exp[-(t/\tau_\alpha)^{\beta_\alpha}] \tag{2}$$

in the time domain, or an appropriate Fourier transform in the frequency domain. The method of determining the local segmental relaxation time, τ_α, and the stretch exponent, β_α, by fitting the experimental data are described in the sections to follow. Recently, it was found that the temperature dependence of τ_α is correlated with β_α. After defining T_g as the temperature at which $\tau_\alpha(T_g)$ is equal to an arbitrary long time, e.g., 10^2 s, it was found that the steepness index,[12]

$$S = \mathrm{d}\,\log \tau_\alpha/\mathrm{d}(T_g/T)|_{T=T_g} \tag{3}$$

also called the fragility index, m,[13] correlates with (1 −

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β_α) when comparing experimental data of different amorphous polymers[12] and other glass-forming substances.[13] SR[9] used the steepness index S to compare the local segmental dynamics of low molecular weight polystyrenes with high moleuclar weight polystyrenes. They found that the steepness index of low molecular weight polystyrene is smaller, or, in other words, the T_g-scaled temperature dependence of the local segmental relaxation is weaker (i.e., less fragile in Angell's classification scheme[14,15]), but the heat capacity change at T_g is larger than its high molecular weight counterpart.

In a section to follow, photon correlation spectroscopy (PCS) data taken on a low molecular weight polystyrene are presented. Afterward, the dynamics of the local segmental motion in the low molecular weight sample obtained by PCS are compared with the following: (1) recoverable creep compliance, $J_r(t)$, data taken previously on the same sample,[5] (2) both PCS and $J_r(t)$ data of high molecular weight PS samples, and (3) the dynamic loss modulus data of low molecular weight polystyrenes obtained by SR. Finally, these results together with the comparison between them for high and low molecular weight samples are interpreted with the help of the coupling model.[16–20]

Experimental Section

Samples of high optical quality are a prerequisite for photon correlation spectroscopic studies in bulk polymers. The polystyrene sample (PS-A67) studied in this work is quite monodisperse with $M_n = 1100$ and $M_w/M_n = 1.03$. It was dissolved in benzene, subsequently the solution was filtered through a Millipore filter into a dust free light scattering cell, and the solvent was removed with the help of a vacuum.

The experimental autocorrelation function was measured with an apparatus equipped with an argon ion laser (Spectra Physics 2020) operating at a wavelength of 488 nm. The incident beam was polarized vertically with respect to the scattering plane, and the scattered light intensity from the sample was collected through a Glan-Thompson polarizer with extinction coefficient better than 10^{-7}. The scattered light was polarized either vertically or horizontally to the scattering plane. An ALV-5000 multibit, multi-τ full digital correlator was used that covered a broad dynamic range from 1 μs to 10^3 s.

Results

The dynamic light scattering experimental correlation functions of the low molecular weight PS-A67 sample were treated in the homodyne limit. The measured intensity autocorrelation function $G(q,t)$ is related to the normalized field correlation function $g(q,t)$ of interest by

$$G(q,t) = A[1 + f|ag(q,t)|^2] \tag{4}$$

Here $q = (4\pi n/\lambda)\,\sin(\theta/2)$ is the scattering vector, n is the refractive index of the bulk polymer, θ is the scattering angle, λ the laser wavelength, f is an instrumental factor calculated by means of a standard solution, a is the fraction of the total scattered intensity associated with density fluctuations with correlation times longer than 10^{-6} s, and A is the baseline at long times. Intensity correlation functions $[G(t)/A - 1]/f$ for six temperatures are shown in Figure 1. The scattering profile of the intensity is stable over the duration of the experiment, and the relatively high value of the experimental $[G(t)/A - 1]/f$ at short times justifies the assumption of homodyne conditions. In fact, the intercept of the correlation functions shown in Figure 1 at short times is close to 1. At each temperature, the correlation function, $ag(q,t)$, can be well-fitted by a Kohlrausch–Williams–Watts (KWW) function,[17,18]

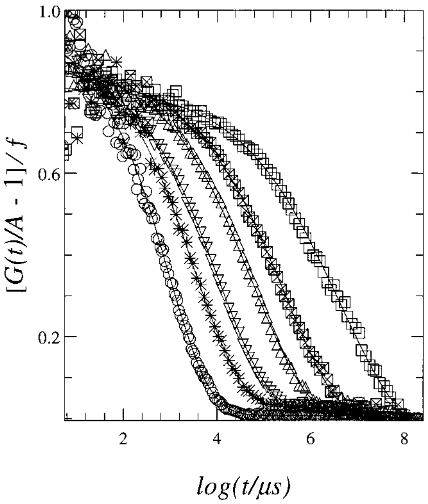

Figure 1. Depolarized intensity correlation functions for PS-A67 at six temperatures, 327, 323, 320, 314, 310, and 305 K from left to right. Solid curves are the KWW fits to the data and the parameters used in the fits are given in Table 1.

Table 1. KWW Exponent β_α, KWW Relaxation Time $\tau_\alpha(T)$, and Average Relaxation Time $\langle\tau_\alpha(T)\rangle = [\Gamma(1/\beta_\alpha)/\beta_\alpha]\tau_\alpha(T)$, Where Γ_Is the Gamma Function of the Low Molecular Weight Polystyrene Sample PS-A67 Obtained by Fitting the Photon Correlation Spectroscopy Data at Different Temperatures T by Equations 4 and 5

T (K)	$\beta_\alpha(T)$	$\log_{10}(\tau_\alpha(T)/\mathrm{s})$	$\log(\langle\tau_\alpha(T)\rangle/\mathrm{s})$
327	0.50	−2.51	−2.21
323	0.47	−2.16	−1.81
320	0.43	−1.48	−1.04
317	0.44	−1.41	−1.01
314	0.40	−0.75	−0.23
310	0.38	0.33	0.92
305	0.36	1.87	2.6

$$ag(q,t) = A_\alpha \exp[-(t/\tau_\alpha)^{\beta_\alpha}] \tag{5}$$

with parameters A_α, τ_α, and β_α that give respectively the contrast, relaxation time, and shape of the local segmental relaxation process. The mean retardation time $\langle\tau_\alpha\rangle = (\Gamma(1/\beta_\alpha)/\beta_\alpha)\tau_\alpha$ and the stretched exponent β_α characterize the longitudinal mechanical response of the local segmental motion determined for seven temperatures can be found in Table 1. The important feature of β_α found in our low molecular weight polystyrene sample PS-A67 is its strong temperature dependence, which has not been seen before in PCS measurements on high molecular weight polystyrenes (PS).[21–23] These previous measurements on high molecular weight PS have found β_α to have a temperature independent value of 0.34.[21,22] On the other hand, β_α for PS-A67 starts out with a much larger value of 0.50 at 327 K (53.8 °C) where $\tau_\alpha(T) = 3.1$ ms, but it decreases monotonically with decreasing temperature to reach the value of 0.36 at 305 K (31.8 °C), where $\tau_\alpha(T) = 74.1$ s. This temperature dependence of β_α from PCS has been seen before in another *low* molecular weight (5000) polymer, poly(methylphenylsiloxane),[24] while on the other hand PCS data of high molecular weight poly(methylphenylsiloxane)[25] show a temperature independent β_α.

A second type of analysis which does not assume any functional form for the correlation functions was also

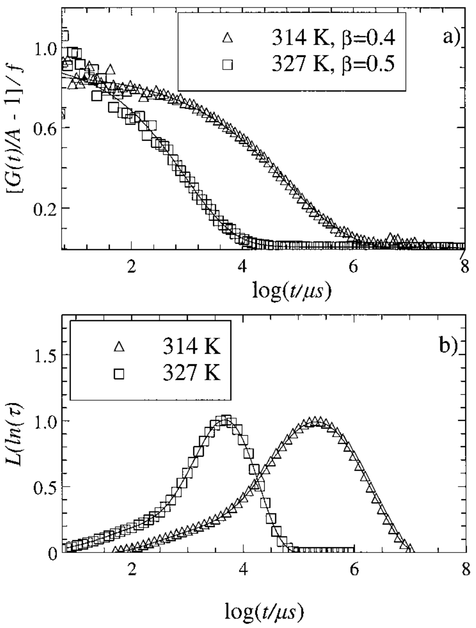

Figure 2. Distribution $L(\log \tau)$ of local segmental retardation times obtained from the ILT analysis (eq 6) of the time correlation data at two temperatures in Figure 1.

made with the use of the inverse Laplace transform (ILT) of the measured time correlation functions using the CONTIN algorithm,[26]

$$ag(q,t) = \int_0^\infty L(\log \tau) \exp(-t/\tau)\, \mathrm{d} \ln \tau \qquad (6)$$

The results of the ILT analysis of the correlation function at two different temperatures (Figure 2a) are illustrated in Figure 2b. The ILT result shows that the retardation spectrum $L(\log \tau)$ broadens continuously as temperature decreases, in agreement with the temperature dependence of β_α found.

Discussion

(a) Recoverable Creep Compliance Data. First, we summarize the information on the local segmental motion deduced from recoverable creep compliance data obtained some time ago on the *same* low molecular weight sample PS-A67[5] and on other high molecular weight polystyrene samples. The contribution of the local segmental to the isothermal recoverable compliance, $J_\alpha(t)$, in the time range of $10^{-0.5} \le t \le 10^6$ s has been determined for high molecular weight PS[5] and is well-fitted[27,28] by the expression

$$J_\alpha(t) = J_g + (J_{s\alpha} - J_g)[1 - \exp(-(t/\tau_\alpha)^{\beta_\alpha})] \qquad (7)$$

Here, τ_α is the temperature dependent retardation time, β_α is a fractional exponent, J_g and $J_{s\alpha}$ are the glassy compliance and the contribution of the local segmental motions to the steady-state recoverable compliances, respectively. At the temperature for which τ_α is about 10^2 s, the parameters in eq 7 have been determined. They are $\beta_\alpha = 0.36$, $J_g = 9 \times 10^{-10}$ Pa^{-1}, and $J_{s\alpha} \approx 3.5 \times 10^{-9}$ Pa^{-1},[27] and the values of these parameters remain approximately the same in a fit to $J_\alpha(t)$ of low molecular weight PS's including PS-A67.[28] Note that the relaxation strength defined by ratio $J_{s\alpha}/J_g$ is about 4. For such *small* relaxation strength of the local segmental motion, numerical calculation of the modulus $G_\alpha(t)$ from the relation $\int_0^t G_\alpha(t')\, J(t - t')\, \mathrm{d}t' = t$,[1] with $J_\alpha(t)$ given by eq 7, can be well-described by

$$G_\alpha(t) = (-J_{s\alpha}^{-1} + J_g^{-1}) \exp[-(t/\tau_\alpha')^\gamma] + J_{s\alpha}^{-1} \qquad (8)$$

with γ approximately the same as β_α and τ_α' only within a factor of 2 the same as τ_α in eq 7.[29] Thus, whichever way the photon correlation spectroscopy result is interpreted, eqs 4 and 5, either as a longitudinal modulus or compliance, it can be effectively compared with $J_\alpha(t)$ in eq 7.

(b) Comparing PCS and Recoverable Creep Compliance Data. When $t = \tau_\alpha$, $J_\alpha(t)$ in eq 7 has the value of 3.06×10^{-9} Pa^{-1}. Therefore, a good approximate estimate of τ_α can be obtained from the creep compliance $J_r(t)$ data of PS-A67[5] by locating the time at which $J_r(t) = 3.06 \times 10^{-9}$Pa^{-1}. In this manner we have determined the shear retardation times τ_α of PS-A67 as well as two high molecular weight polystyrenes, PS-A25 and PS-L5, with $M_v = 46\,000$ and $M_v = 122\,000$, respectively. The creep compliance data of these high molecular weight polystyrenes have previously been measured.[1,5,30,31] The temperature dependencies of τ_α for PS-A67, PS-A25, and PS-L5 are all well-fitted to the Vogel–Fulcher or the equivalent WLF equation. If T_{ref} is defined as the reference temperature at which $\tau_\alpha(T_{\mathrm{ref}})$ is equal to 100 s, we find that T_{ref} is equal to 313.15 K (40 °C) for PS-A67, 370.15 K (97 °C) for PS-A25, and 370.20 K (97.05 °C) for PS-L5. The same procedure when applied to τ_α for PS-A67 obtained from PCS measurement leads us to find a $T_{\mathrm{ref}} = 304.3$ K (31.1 °C). There is difference of about 9 K for T_{ref}'s obtained from PCS and shear compliance measurements on the same sample, PS-A67. Such a difference is not unexpected because after all PCS measures a longitudinal response which is not the same as the shear compliance.

This difference in T_{ref}'s from PCS and creep compliance for the low molecular weight PS-A67 is small compared with the difference (about 60 K) between them and the T_{ref}'s of the two high molecular weight polystyrenes. Despite the difference, large and small, between the T_{ref}'s, the temperature dependences of the different τ_α's can be compared altogether in semilogarithmic plots of log τ_α against the respective scaled inverse temperature, (T_{ref}/T).[12,13,32] Different glass-forming liquids may have log τ_α change more rapidly with (T_{ref}/T) as (T_{ref}/T) approaches the value of unity from below, i.e., as the reference temperature is approached from above. Angell[14,15] introduced the terms "fragile" and "strong" to describe the varied dependences of log τ_α on (T_{ref}/T). More fragile (stronger) liquids have a more (less) rapid change of log τ_α as $(T_{\mathrm{ref}}/T) \rightarrow 1$. According to Angell,[14,15] fragile or strong behavior is related to the topology of the free energy hypersurface governing the structural relaxation. Another interpretation based on the coupling model[12,13,32] is that the more rapid change of log τ_α with (T_{ref}/T) results from greater intermolecular constraints (i.e., degree of cooperativity) between the basic molecular units in motion. Even at an intuitive level, it is clear that a higher degree of cooperativity is associated with a higher degree of dynamic heterogeneity[33-36] and hence a larger dispersion of the local segmental motion which means a smaller β_α and $(1 - n_\alpha)$ in eqs 5 and 7, respectively. This view is supported by the correlation between the steepness S of the temperature variation of log τ_α at $(T_{\mathrm{ref}}/T) = 1$ and β_α found in amorphous polymers[12,13,32] and also in nonpolymeric glass-formers.[13]

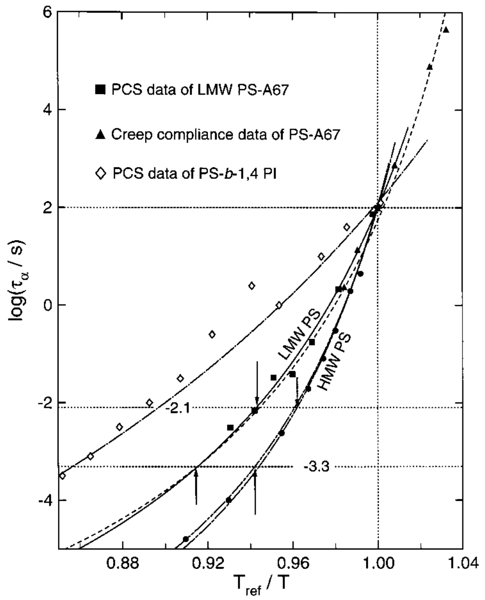

Figure 3. Plots of log τ_α and VFTH fit against the respective (T_{ref}/T) of the PCS data of PS-A67 (filled squares and solid curve) and the creep compliance data of the low molecular weight (LMW) PS-A67 (filled triangles and dashed curve) and the high molecular weight (HMW) PS-A25 (filled circles and the long-dashed−double-short-dashed curve). Only the T_{ref}-scaled VFTH fit to the data of the high molecular weight PS-L5 is shown as the long-dashed−short-dashed curve. Plot of log τ_α of the PS component and VFTH fit against (T_{ref}/T) from the PCS data (see Figure 4) of the poly(styrene-*b*-1,4-isoprene) block copolymer (open diamonds, dashed−dotted curve).

The plots of log τ_α against the respective (T_{ref}/T) of the PCS data of PS-A67 and the creep compliance data of PS-A67 and the two high molecular weight polystyrenes, PS-A25 and PS-L5, are shown in Figure 3. For PS-A67, the variation of log τ_α with (T_{ref}/T) from PCS data (filled squares) and creep compliance data (filled triangles) agree well. The dashed curve corresponding to a Vogel−Fulcher−Tammann−Hesse (VFTH) fit to the creep compliance data of PS-A67 given before in ref 5, and it fits also the PCS data at higher temperatures. The full curve comes from the VFTH fit to the PCS data in Table 1 which is given by $\log(\tau_\alpha(T)/\mathrm{s}) = -10.0 + [426.7/(T - 268.7)]$. The variation of log τ_α with (T_{ref}/T) from creep compliance data of the two high molecular weight polystyrenes agree very well. The experimental data of PS-A25 are shown as filled circles and the T_{ref}-scaled VFTH fit to them is the long-dashed−double-short-dashed curve. Only the T_{ref}-scaled VFTH fit to the data of PS-L5 is shown in Figure 3 as the long−short dashed curve. By comparing them above and below (T_{ref}/T) = 1, the T_{ref}-scaled temperature dependence of log(τ_α/s) of PS-A67 is clearly weaker than that of PS-A25 and PS-L5, confirming the findings of SR from shear modulus measurements that low molecular weight polystyrenes are less fragile.[9] The values of log τ_α at any fixed value of (T_{ref}/T) between our 1100 molecular weight sample PS-A67 is nearly the same as those obtained by SR on a sample with a similar molecular weight (760). Santangelo and Roland[9] defined their T_{ref} as the temperature at which log(τ_α/s) = 2, exactly like what we have done here. There is also similar agreement between our results and theirs for the high molecular weight samples.

(c) Comparing PCS with Shear Modulus Data. An empirical correlation between fragility and the KWW exponent β_α has been established for amorphous polymers[12,13,32] and also for nonpolymeric glass-formers.[13] From this correlation and the fact that low molecular weight polystyrene is less fragile than high molecular weight polystyrene, one would expect that the former should have a larger β_α or narrower dispersion for the local segmental motion than the latter. However, the complex dynamic shear modulus, $G^*(f)$, data measured in the frequency range of $1 > f > 10^{-5}$ Hz by SR on many polystyrene samples with a wide range of molecular weights have led them to conclude that the dispersion of the local segmental relaxation is almost independent of molecular weight. Hence the correlation seems to break down in polystyrenes. Isothermal data taken by SR that determines the dispersion of the local segmental motions were obtained at a temperature for which the peak of $G''(f)$, the imaginary part of $G^*(f)$, is located at a frequency near the middle of the experimental frequency window, e.g., $10^{-2.5}$ Hz. This frequency corresponds approximately to a relaxation time of 10^2 s. Our PCS data on PS-A67 at 305 K (31.8 °C) has a comparable relaxation time, and the dispersion is characterized by $\beta_\alpha = 0.36$ (see Table 1). Recoverable creep compliance data of Plazek and co-workers[5] on polystyrene were taken in the time range of $10^{-0.5} < t < 10^6$ s, complementary to the frequency range investigated by SR. As we have discussed earlier in connection with eq 5, the contribution of the local segmental motions to the isothermal recoverable compliance, $J_{s\alpha}(t)$, when the retardation time τ_α is equal to approximately 10^2 s, also has $\beta_\alpha = 0.36$ for both low molecular weight polystyrenes including PS-A67 and also for high molecular weight samples including PS-A25 and PS-L5. Therefore, although the PCS dispersion is temperature dependent, our PCS data of PS-A67 at 305 K (31.8 °C) and the $J_\alpha(t)$ data of *all* molecular weights with retardation times τ_α of approximately 10^2 s, have nearly the same dispersion or β_α value of 0.36. This finding confirms the other result of SR that their $G''(f)$ peaks have the same shape independent of the molecular weight of the polystyrenes. At this point, it seems apparent that the correlation between the steepness index S and $(1 - \beta_\alpha)$[12,13,32] breaks down for polystyrenes of low and high molecular weights. In the next section, we shall discuss the other PCS data of PS-A67 taken at temperatures higher than 305 K (31.8 °C), having relaxation times τ_α much shorter than 10^2 s. These PCS data will be utilized to reconcile the apparent breakdown of the correlation between β_α and the fragility[12,13,32] inferred from the low and high molecular weight polystyrenes shear modulus data taken by Santangelo and Roland[9] and also the shear compliance measurements.[5] In addition, the PCS data will shed more light on the cause of the reduction in T_g and the change in local segmental dynamics of low molecular weight polymers.

Interpretation

(a) Temperature Dependence of b_a. The photon correlation spectroscopy (PCS) data taken in the time range of $10^{-6} < t < 10^3$ s provides information on the dynamics of local segmental motion that are inaccessible by mechanical measurements[5,9] confined to longer times (or lower frequencies). Such information on PS-A67 are given by PCS measurements and the fits by eqs 4−6 at temperatures above 305 K (31.8 °C). The results given in Table 1 indicate that β_α is strongly temperature dependent, increasing monotonically with temperature from 0.36 at 305 K (31.8 °C) to 0.50 at 327 K. This temperature sensitivity of β_α, which corresponds to a narrowing of the dispersion with increasing temperature, was not found in high molecular weight polystyrene.[21−23] The same difference, although to a lesser degree, has been found in low and high molecular weight poly(methylphenyl siloxane),[24,25] indicating that the effect can be more general. However, the effect is only observed in polymers which are not very flexible and have higher intermolecular cooperativity or smaller β_α values such as polystyrene and poly(methylphenyl siloxane). The very flexible poly(dimethylsiloxane) with a lower degree of cooperativity (larger β_α) than polystyrene and poly(methylphenylsiloxane) has both β_α and the T_{ref}-scaled temperature dependence of τ_α being independent of molecular weight.[6] It is worthwhile to point out that the fragility index, m, decreases and β_α increases when going from polystyrene to poly(methylphenylsiloxane) and to poly(dimethylsiloxane).[12,13,32] Thus, from the trend shown by the three polymers it seems that the effect diminishes with a decreasing degree of cooperativity (i.e., decreasing m and increasing β_α).

If the effect is general for polymers with a higher degree of cooperativity, then the cause must come from a generic property of linear polymers with a very low degree of polymerization. The most obvious generic property of low molecular weight polymers is the increasing number density of chain ends as the molecular weight decreases. Repeat units at or near the chain ends have higher mobility than the inner repeat units. This difference can be rationalized in the free volume model, the entropy model, and the coupling model by the chain ends having, respectively, excess free volume, excess configurational entropy, and deficient intermolecular constraints (or reduced coupling parameter). In the coupling model, the degree of intermolecular cooperativity is measured by the coupling parameter, n_α, which is exactly $(1 - \beta_\alpha)$. The difference in mobility between chain ends and inner repeat units is expected to be larger for polymers that have greater intermolecular coupling or smaller β_α (in the high molecular weight regime where chain ends are virtually absent) because greater intermolecular cooperativity results in much lower mobility of the inner repeat units. This expected trend explains why the effect diminishes in the order of polystyrene, poly(methylphenylsiloxane), and poly(dimethylsiloxane). Poly(dimethylsiloxane) has ether backbone linkages, which make the chain very flexible, and low intermolecular cooperativity and a large β_α value of 0.57 [6] compared with 0.36 for polystyrene[21,22,27,28] and 0.44 [25] for poly(methylphenylsiloxane) whose cooperativity compared with poly(dimethylsiloxane) is enhanced due to the replacement of one methyl by the bulkier phenyl group.

(b) Spectral Broadening Caused by Blending Chain Ends with Inner Units. A low molecular weight polymer in which there is a nonnegligible number density of chain ends can be considered as a miscible blend of chain ends and inner repeat units. The local segmental dynamics in miscible binary polymer blends and copolymers have been studied extensively both experimentally[37−41] and theoretically.[42−44] Concentration fluctuations of the components in the blend engender a distribution of local environments for local segmental motion (LSM) of any component. Dynamic heterogeneity due to intermolecular cooperativity contributes one source of broadening to the dispersion of the LSM. In the coupling model[17,27,28,31] this broadening is represented by a stretched exponential function, $\exp[-(t/\tau_\alpha)^{1-n_\alpha}]$, for each component. The distribution of local environments caused by concentration fluctuations further broadens the dispersion because a weighted sum of $\exp[-(t/\tau_\alpha)^{1-n_\alpha}]$'s over the distribution $\{n_\alpha\}$ has to be considered.[38,39] A characteristic of this broadening by concentration fluctuation is that it increases with decreasing temperature[37−44] because a longer time response comes from fluctuation having a larger n_α's and its shift factor has a stronger temperature dependence.[38,39,42,43] The combined effect is a broader dispersion whose width increases with decreasing temperature. This feature seems to be a general property of blends because it has been observed repeatedly in several blends[37−41] and can be explained by the coupling model generalized to blends.[42,43] In the coupling model description of component dynamics in a blend, the coupling parameter n_α of any one of the components has a distribution of values. The component having greater intermolecular constraints or larger n_α in the pure state will have all its distributed values of n_α reduced in the blend. This is supported by the experimentally observed reduction in the fragility of the T_{ref}-scaled temperature dependence of the most probable relaxation time of that component.[38,39,42,43] Applying to low molecular weight polymers, now considered as blends of chain ends and inner repeat units, this general feature readily explains why the dispersion of LSM found in PS-A67 by PCS is temperature dependent, broadening with decreasing temperature (see Figures 1 and 2 and the decrease of β_α with temperature decrease in Table 1), and why the fragility of PS-A67 is lower than that of high molecular weight polystyrenes (see Figure 3).

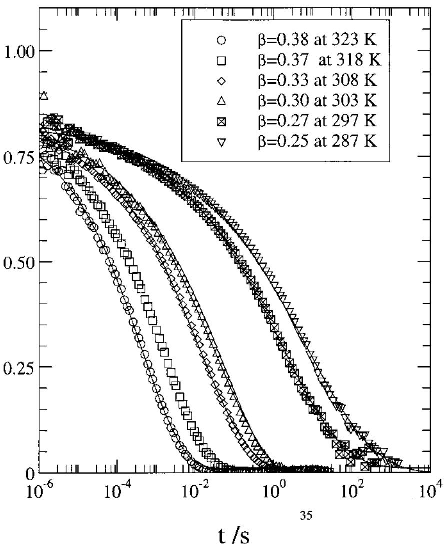

Figure 4. Depolarized intensity correlation functions for the poly(styrene-*b*-1,4-isoprene) block copolymer at six temperatures. Solid curves are the KWW fits to the data, and the β parameters used in the fits are given in the inset.

To fortify our consideration of low molecular weight polystyrene as a blend of chain ends and inner repeat units, we show in Figure 4 some depolarized intensity correlation functions data from photon correlation spectroscopy for six temperatures of a poly(styrene-*b*-1,4-isoprene) block copolymer in the disordered state above the order−disorder transition temperature. A portion of these data has been previously published in ref 41. The total molecular weight of the copolymer is $M_n =$

3930, and the molecular weight of the PS block itself is equal to 2830. These PCS data are contributed primarily by the local segmental motion of PS in the copolymer.[41] In this copolymer blend, just like PS-A67 (Figures 1 and 2), the dispersion broadens with decreasing temperature, which is evident by inspection of the curves in Figure 4 and the temperature dependence of β_α of the forced KWW fits to the data. Like before, taking again $T_{ref} = 280.1$ K (6.9 °C) as the temperature at which the relaxation times τ_α in the KWW fits is equal to 10^2 s, the T_{ref}-scaled temperature dependence of the relaxation times together with its VFTH fit are plotted in Figure 3. There is even a less rapid change of log τ_α with $(T_{\rm ref}/T)$ of PS in the block copolymer than in PS-A67. In the block copolymer, the more mobile PI repeat units, present themselves in much larger concentration than chain ends in PS-A67, naturally have larger effects including a lower T_{ref}, a broader dispersion and larger increase with temperature decrease, and a less rapid T_{ref}-scaled temperature dependence of the relaxation times. Thus, except for quantitative differences which can be understood, the PCS data of the block copolymer blend and PS-A67 exhibit the same effects which result from a combination of concentration fluctuations and lower intermolecular coupling by the presence of a more mobile component, chain ends in PS-A67 and the PI block in the poly(styrene-*b*-1,4-isoprene) block copolymer. In short, because the end units are more loosely coupled than internal repeat units, a temperature dependent copolymer-like broadening of the dispersion occurs.

(c) Actual Value of the Coupling Parameter. The family of KWW functions in eq 5 is so flexible that they could still provide good fits to the dispersion in some blends such as PS-A67 and poly(styrene-*b*-1,4-isoprene). The values of β_α obtained in the fits using eq 5 characterize the dispersion of the blend and they are temperature dependent, decreasing with decreasing temperature (see Table 1). At the highest temperature accessible by the PCS measurements of PS-A67, β_α assumes the largest value of 0.50. Although the broadening due to concentration fluctuation is diminished at higher temperatures,[37−44] we expect that this β_α value of 0.50 is still smaller than the exponent β_α in the KWW function, $\exp[-(t/\tau_\alpha)^{\beta_\alpha}]$, that represent the broadening due to intermolecular cooperativity alone. Thus, the PCS experimental data provides a bound, $\beta_\alpha \geq 0.50$, on the actual value of β_α in PS-A67. The coupling model identifies the coupling parameter $\hat{n}_\alpha$ with $(1 - \beta_\alpha)$, and hence we have the bound

$$\hat{n}_\alpha \leq 0.50 \tag{9}$$

for the most probable coupling parameter in PS-A67. Without further experimental work beyond the present PCS measurement, it is not possible to remove the contribution to broadening due to concentration fluctuations and to determine the actual value of $\hat{n}_\alpha$. So, at this time we can only give some estimates of the reduction of the local segmental relaxation time caused by the change of coupling parameter from $n_{\rm HMW} = 0.64$ in high molecular weight (HMW) polystyrenes to some hypothetical values of $\hat{n}_\alpha$ in PS-A67, satisfying the bound given by eq 9.

(d) Estimating the Reduction in Glass Temperature. We assume that at the glass temperature of high molecular weight PS, $T_{\rm g,HMW} = 370$ K (96.8 °C), $\tau^*_{\rm HMW}(T_{\rm g,HMW})$ is equal to 10^2 s. With this value of $\tau^*_{\rm HMW}$, $n_{\rm HMW} = 0.64$, $t_{\rm c} = 2 \times 10^{-12}$ s, and a result of the coupling model[16−20,27,28]

$$\tau^*_{\rm HMW} = [t_{\rm c}^{\,-n_{\rm HMW}}\tau_{\rm o}]^{1/(1-n_{\rm HMW})} \tag{10}$$

the value of the primitive (i.e. without the effect of intermolecular cooperativity) relaxation time,

$$\tau_{\rm o}(T_{\rm g,HMW}) = 10^{-6.8}\ {\rm s} \tag{11}$$

is obtained. The quantity $t_{\rm c}$ in eq 10 is the crossover time from primitive relaxation, $\exp(-t/\tau_{\rm o})$, to intermolecularly coupled slow relaxation, $\exp[-(t/\tau^*_{\rm HMW})^{1-n_{\rm HMW}}]$, of the coupling model. In polymers including poly(vinyl chloride) (PVC),[45] polybutadiene (PB), and polyisoprene (PI),[46] analyses of quasielastic neutron scattering data have determined the value of $t_{\rm c} = 2 \times 10^{-12}$ s given. By comparing simulation data of polyethylene by Takeuchi and Roe[47] with the coupling model results,[48] a $t_{\rm c}$ of similar magnitude has been deduced. Short-time molecular dynamics simulation data of polyethylene by Roe[49] over the time range of $10^{-14} < t < 10^{-9}$ s show directly a crossover from a fast process of a diffusive nature consistent with the primitive relaxation to a slower process well-approximated by $\exp[-(t/\tau^*_{\rm HMW})^{1-n_{\rm HMW}}]$. Molecular dynamics and quasielastic neutron scattering experiment have been performed on polyethylene in the picosecond and shorter time regime[50] and a crossover of behavior at $t_{\rm c}$ seems to be apparent. Recently, Roe has also performed molecular dynamics simulation of atactic polystyrene and found qualitatively the same result.[51] In the polymers poly(vinyl chloride), polyisoprene, polybutadiene, polyethylene, and polystyrene as well as in a van der Waals liquid *o*-terphenyl,[52] $t_{\rm c}$ lies between 1 and 2 ps. These principal results of the coupling model are also obtained theoretically from simple models that have anharmonic interactions.[19,20]

Since $\tau_{\rm o}$ is the local segmental relaxation time in the absence of intermolecular interaction, it would be the same for high or low molecular weight polystyrene at the same temperature provided other thermodynamic variables including the specific volume remain the same. From the work of Fox and Flory,[2,3] the specific volume of a low molecular weight polymer is larger than the high molecular weight counterparts. Thus, unless the difference in specific volume is just a *consequence* of the difference in the intermolecular and intramolecular (bonded) interactions in high and low molecular weight polymers and have no effect on $\tau_{\rm o}(T_{\rm g,HMW})$, we can expect that $\tau_{\rm o}(T_{\rm g,HMW})$ will be even shorter in low molecular weight PS (reflecting the larger specific volume) than what we shall deduce from HMW polystyrenes using the coupling model (eq 10). We ignore, for the time being, any possible change in $\tau_{\rm o}(T_{\rm g,HMW})$ caused by the difference in specific volume and consider first the effect due solely to the reduction of the coupling parameter n_α in low molecular weight PS (eq 9) from the high molecular weight PS value of $n_{\rm HMW} = 0.64$. With the same values of $\tau_{\rm o}(T_{\rm g,HMW}) = 10^{-6.8}$ s and $t_{\rm c} \approx 2 \times 10^{-12}$ s for $\hat{n}_\alpha = 0.49$, we can calculate the value of relaxation time of PS-A67 at $T_{\rm g,HMW} = 370$ K (96.8 °C), by

$$\tau^*_{\rm A67}(T) = [t_{\rm c}^{\,-\hat{n}_\alpha}\tau_{\rm o}]^{1/(1-\hat{n}_\alpha)} \tag{12}$$

which is just another form of eq 10 now applied to PS-

A67. The value obtained for $\tau^*_{A67}(T_{g,HMW} = 370\ K)$ is $10^{-2.1}$ s, which is about 4 orders of magnitude faster than $\tau^*_{HMW}(T_{g,HMW}) = 10^2$ s. In principle, at T below $T_{g,HMW}$, we can use the VFTH fit to the temperature dependence of $\tau^*_{HMW}(T)$ and eq 10 to calculate $\tau_o(T)$ and then eq 12 to obtain $\tau^*_{A67}(T)$. This method will give us directly the theoretical glass temperature $T_{g,A67}$ of PS-A67 at which $\tau^*_{A67}(T_{g,A67})$ will attain the value of 10^2 s. However, this method is not dependable because long extrapolation using the rapidly varying VFTH fit to temperatures far below $T_{g,HMW}$ is subject to large errors. Therefore, instead we shall use the T_{ref}-scaled temperature dependence of the local segmental relaxation time τ_α from our current PCS data on PS-A67 and τ^*_{A67}(370 K, 96.8 °C) $= 10^{-2.1}$ s to extrapolate the temperature dependence of $\tau^*_{A67}(T)$ in order to determine the glass temperature $T_{g,A67}$ at which $\tau^*_{A67}(T_{g,A67})$ will attain the value of 10^2 s. The procedure we used is first to locate the value $(T_{ref}/T)|_{\tau_\alpha=\tau^*_{A67}}$ of T_{ref}/T at which τ_α from the VFTH fit to the PCS data of PS-A67 is exactly the same as τ^*_{A67}(370 K, 96.8 °C) $= 10^{-2.1}$ s. The location of $(T_{ref}/T)|_{\tau_\alpha=\tau^*_{A67}(370\ K)}$ is indicated by the position of the vertical arrow in Figure 3 pointing downward toward the T_{ref}-scaled curves of PS-A67 and the horizontal line defined by the y-value equal to -2.1. Then, $T_{g,A67}$ is calculated by the expression

$$T_{g,A67} = 370(T_{ref}/T)|_{\tau_\alpha=\tau^*_{A67}(370\ K)} \quad (K) \qquad (13)$$

We find $T_{g,A67} = 349$ K (75.8 °C) which is a reduction of 21 K from $T_{g,HMW}$.

The value of $\hat{n}_\alpha = 0.49$ used to calculate $T_{g,A67}$ in the previous paragraph is equal, within experimental error, to the upper bound of the actual coupling parameter in PS-A67 established by eq 9. In all likelihood, the actual value of $\hat{n}_\alpha$ is smaller because there must be some residual contribution to the broadening of the dispersion from concentration fluctuations even at 327 K (53.8 °C), the highest temperature of PCS measurement (see Table 1). We take some possible, though at this time hypothetical, values of $\hat{n}_\alpha$ and see what $T_{g,A67}$'s they will give. For example, if $\hat{n}_\alpha = 0.40$, then $\tau^*_{A67}(370\ K) = 10^{-3.3}$ s and the locations of $(T_{ref}/T)|_{\tau_\alpha=\tau^*_{A67}(370\ K)}$ are given by the arrow pointing vertically upward and toward the T_{ref}-scaled curve and the horizontal line. The $T_{g,A67}$ equal to 338.3 K (65.1 °C) are obtained from eq 13 when using the T_{ref}-scaled temperature dependence of PS-A67. The smaller value of 338.3 K (65.1 °C) is still larger than, but in closer agreement with, the experimental T_{ref} or T_g of PS-A67, which is at 313 K (39.8 °C). It is quite possible that the remaining difference is due to the effect of a larger specific volume of a low molecular weight polystyrene such as PS-A67 than HMW polystyrenes as found by Fox and Flory[2,3] experimentally. Even though the exact magnitude is still uncertain, we can conclude that a significant portion of the reduction of the glass temperature in low molecular weight polystyrene is due to a reduction in intermolecular coupling (i.e., the coupling parameter in the coupling model) by the presence of chain ends. Albeit the limit $\hat{n}_\alpha = 0$ cannot be reached in low molecular weight polystyrene even when chain ends become preponderant because there is still intermolecular coupling between the monomers or oligomers, it is interesting to see what is the lowest T_g of PS-A67 that is predicted by eq 12 if we put $\hat{n}_\alpha$ therein equal to zero; i.e., cooperativity totally vanishes. In this case, τ^*_{A67}(370 K, 96.8 °C) $= \tau_o(T_{g,HMW}) = 10^{-6.8}$ s (see eq 12). Again, using the T_{ref}-scaled temperature dependencies of PS-A67, $(T_{ref}/T)|_{\tau_\alpha=\tau^*_{A67}(370\ K)} = 0.76$, and from eq 13 the lowest T_g is 281 K (7.8 °C), which is now even smaller than the actual T_g of PS-A67. This totally academic estimate ensures that reduction in intermolecular coupling by chain ends could be sufficiently potent to account for a major portion of the reduction of T_g seen in low molecular weight polystyrenes.

We have allowed for the possibility that the increase in specific volume can be responsible for part of the reduction in the glass temperature of low molecular weight polystyrenes. Nevertheless, we emphasize that the other part of the reduction in T_g caused by a decrease of the coupling parameter in the coupling model is necessary in order to explain also the fragility change (Figure 3) and the temperature dependence of the dispersion (Figures 1 and 2). Furthermore, without the coupling model, specific volume or free volume considerations alone cannot explain the viscoelastic anomalies found in high and low molecular weight polystyrenes and other amorphous polymers.[27,28,30,31]

(e) Reconciling with the Data of Santangelo and Roland. Our PCS data on PS-A67 at 305 K (31.8 °C) with $\log[\langle\tau(T)\rangle/s] \approx 2$ together with the analysis of recoverable creep compliance data of PS-A67 (see eq 7 and the discussions following it) confirmed the observation of SR by dynamic modulus measurement[9] in a compatible time/frequency range that the breadth of the local segmental relaxation is independent of molecular weight. In other words, the values of β_α used to fit PCS data on PS-A67 at 305 K (31.8 °C) and mechanical data by the KWW function are the same, about 0.36, independent of chain length as long as $\log[\tau_\alpha(T)/s] \approx 2$. On the other hand, as first shown by SR and also confirmed here, the T_{ref}-scaled temperature dependence of the local segmental relaxation time of the low molecular weight polystyrene is weaker (or less fragile) than HMW polystyrenes. These results have led SR to state that "...PS is a rare exception to the well-known correlation between the temperature dependence and the breadth of the segmental relaxation function.... This correlation is predicted by the coupling model of relaxation." The PCS data of PS-A67 can resolve this apparent violation. First, from an entirely experimental point of view, the PCS data of PS-A67 show that, unlike HMW polystyrenes, the breadth of the dispersion is strongly temperature dependent. Second, from the suggestion that concentration fluctuations due to blending of chain ends and inner repeat units cause additional broadening, the actual breadth of the dispersion of PS-A67 contributed by intermolecular coupling and cooperativity is less than that directly taken from the measurements. As a consequence of this interpretation, the PCS data enable the establishment of the upper bound on the coupling parameter $\hat{n}_\alpha$ for PS-A67 given by eq 9. The coupling parameter of low molecular weight polystyrenes is then smaller than that of the HMW polystyrenes. Hence, the coupling model prediction that a glass-former having a larger coupling parameter has a stronger T_{ref}-scaled temperature dependence of the local segmental relaxation time (i.e., a larger S) remains valid also for low and high molecular weight polystyrenes.

There are other ways of reducing the T_g of a polymer. These include (1) diluting the polymer with a solvent[53,54] and (2) making it into a thin freely standing film.[55,56] In case 1, dielectric data of poly(vinyl chloride) solutions has shown the KWW exponent increases and the coupling parameter decreases with dilution. Also, the fragility decreases with dilution. The presence of the solvent mitigates the intermolecular constraints between local segmental motions in different chains or different parts of the same chain, and the experimentally observed decrease of the coupling parameter is expected conceptually. In case 2, dramatic reduction of the glass temperature, T_g, in freely standing polymer thin films has been found by Forrest et al.[55,56] when the thickness of the film becomes approximately smaller than the average end-to-end distance of the unperturbed polymer chains. The reduction of the glass temperature has been attributed to a reduction of the coupling parameter caused by a combination of (1) induced orientations from chain confinement, (2) reduction of cooperativity length scale, and (3) mitigation of intermolecular constraints near free surfaces in thin films.[57] In a forthcoming paper we shall show that the reduction of T_g of small-molecule glass-forming liquids in 2.5 nm pores can be explained also by a decrease of the coupling parameter due to the pore size being smaller than the cooperative length scale of the liquid in the bulk state.

Conclusion

The measurement of local segmental motion in low molecular weight polystyrene by photon correlation spectroscopy in the time window of $1\ \mu\text{s} \leq t \leq 10^3$ s has enabled us to show that the spectral dispersion is temperature dependent, in contrast to the high molecular weight counterpart. This difference is attributed to the preponderance of chain ends in low molecular weight polystyrene which mitigates the constraints between the inner repeat units and reduces their degree of cooperativity or the coupling parameter in the coupling model. We found from our PCS data and recoverable creep compliance data of Plazek and O'Rourke on the same sample that the fragility of low molecular weight polystyrene is lower than that of high molecular weight polystyrene, confirming the experimental fact discovered by Santangelo and Roland by dynamic modulus measurements. Considering the low molecular weight polymer as a miscible blend of chain ends and inner repeat units, analysis of the PCS data led us to the conclusion that the coupling parameter of local segmental motion in low molecular weight polystyrene is significantly reduced from its value for high molecular weight polystyrene. Thus, the correlation between fragility and the coupling parameter hold also when considering polystyrenes with widely different molecular weights. The reduction of the coupling parameter also accounts for at least part of the decrease of the glass temperature of low molecular weight polystyrenes. It would be interesting to carry out the same work reported in this paper on low molecular weight cyclic polystyrene samples where there is an absence of chain ends.

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