Local Segmental Relaxation in Bidisperse Polystyrenes

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ABSTRACT: Dynamic mechanical results are reported for segmental relaxation of mono-disperse polystyrenes (PSs) with molecular weights of 0.7, 3, 18, and 104 kg/mol and bidisperse PSs created from blending pairs of these materials. The data for the mono-disperse polymers confirm previous findings; namely, there is an increase in the glass-transition temperature normalized temperature dependence of the segmental relaxation times (fragility) with increasing molecular weight, along with a breakdown of the correlation between the fragility and the breadth of the relaxation function. For both the monodisperse and bidisperse PSs, the glass-transition temperature is a single function of the average number of chain ends, independent of the nature of the molecular weight distribution. It is also found that these materials exhibit fragilities that uniquely depend on the number-average molecular weight, that is, on the concentration of chain ends. In blends with linear PS, cyclic PS with a low molecular weight behaves as a high polymer, similar to its neat behavior, reflecting the overriding importance of chain ends. © 2004 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 42: 2604–2611, 2004

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INTRODUCTION

Various properties of polymers, such as the glass-transition temperature (T_g) and the strength and modulus of rubbery networks, are influenced by the concentration of chain ends.[1] In high polymers the concentration is negligible; hence, the molecular weight effects are usually negligible. Generally, the molecular weight effects are noticeable only for molecular weights below about 1 kg/mol. (We do not refer to properties such as the viscosity and rubbery plateau length, which depend on the length of the chains per se, rather than on the number of chain ends.) Quantifying

the role of chain ends in conferring additional free volume and configurational entropy, and thus modifying the T_g and segmental relaxation properties, can offer insights into relaxation processes in polymers. Of course, the volume and entropy are also governed by the temperature. However, temperature changes are accompanied by changes in thermal energy, which complicates the analysis, requiring sorting out of the effects of volume and thermal energy on the segmental dynamics.[2–5] Based on the now discredited idea that the T_g represents an isofree volume state, Fox and Flory (FF)[6] derived a well-known expression for the variation of the T_g with the number-average molecular weight (M_n) of linear polymers

$$T_g = T_{g,\infty} - k_{FF}/M_n \qquad (1)$$

in which $T_{g,\infty}$ is the glass-transition temperature in the absence of chain ends and k_{FF} is a polymer-

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specific constant that depends on the chemical nature of the chain end groups.[7,8] An empirical expression that is more accurate for low molecular weights is due to Ueberreiter and Kanig (UK)[9]

$$T_g^{-1} = T_{g,\infty}^{-1} + k_{UK}/M_n \qquad (2)$$

where the constant k_{UK} depends on the nature of the end group. Using approaches not bound to free volume ideas, alternative expressions have been derived.[10,11] However, these offer no advantage in describing experimental T_g versus M_n data for linear polymers. A modification of eq 1, whereby the last term is multiplied by the junction functionality, has been used to analyze the T_g of 4- and 6-arm star polystyrenes (PSs)[12] whereas a similar modification accounting for the generation number has been applied to dendrimers.[13] The implication of studies of branched polymers is that the concentration of chain ends governs the glass-transition temperature. In contrast, Kisliuk et al.[14] recently reported that the T_g of 1,4-polybutadienes, including 4-, 8- and 12-arm stars, depended only on the M_n, not on the degree of branching. Such a result appears to minimize the role of chain ends. However, the results of Kisliuk et al.[14] may reflect two competing effects, in which the contribution of chain ends is countervailed by the constraining effect of the multifunctional branch point from which the arms of the star molecule originate.[12]

The effect of temperature on the local segmental relaxation times (τ) is popularly quantified in terms of the fragility, or T_g-normalized temperature dependence,[15,16]

$$m = \frac{d\log(\tau)}{d(T_g/T)}\Big|_{T=T_g}$$

In analyzing polymer dynamics, the appropriate definition of T_g is the temperature at which the relaxation time assumes some arbitrary value (e.g., 100 s). For some polymers, such as poly(dimethylsiloxane),[17] poly(phenylmethylsiloxane),[18] and poly(propylene oxide),[19] the fragility is independent of the molecular weight; for propylene glycol oligomers,[20] poly(vinylpyridine),[21] and PS the m increases with chain length. In particular, PS has been the focus of several studies, because of conflicting results in the literature.[22,23] However, mechanical spectroscopy,[24] dynamic light scattering,[25] thermal analysis,[26] and dielectric spectroscopy[27] have demonstrated unambigu-

ously that for $M_n < 1$ kg/mol the fragility decreases with decreasing chain length. The appeal of fragility as a means to characterize temperature dependences arises from its correlation with the shape of the segmental relaxation function (or the α dispersion in dielectric spectra), as shown for many molecular and polymeric glass formers.[28,29] There are exceptions to this correlation,[29,30] and PS is one such example. The shape of the segmental relaxation peak measured mechanically[24] or dielectrically[27] is invariant to the molecular weight, despite the chain length dependence of m.

For properties whose molecular weight dependence is solely a function of chain ends, studies of cyclic polymers are relevant because they are analogous to infinite molecular weight linear chains. In actuality, cyclic molecules form a compact structure and lack the configurational freedom of linear polymers.[31–33] We recently showed that both the T_g and m values for cyclic PS were equivalent to the high molecular weight limiting values of the linear polymer, reflecting the importance of chain ends on these two properties.[34] In the present work we vary the concentration of chain ends by blending PSs of low and high molecular weight, including a blend containing a cyclic PS. Such bidisperse polymer blends have been studied previously to examine terminal relaxation (reptation)[35,36] and orientational coupling in polymers.[37,38] An early study determined glass-transition temperatures from thermal expansivity measurements on bidisperse PS blends.[9] Previous works have also used the T_g for blends of chemically dissimilar polymers as means to assess the interaction between the components.[39–42] Herein, we study PS blends to examine the effect of chain ends on both the glass-transition temperature and fragility. It is known that the segmental relaxation times in PS are governed by both volume and thermal energy, with the latter exerting a somewhat stronger influence.[3] In these bidisperse blends, the only consequence of blending is to alter the concentration of chain ends and thereby change the free volume and configurational entropy.

EXPERIMENTAL

Atactic PS standards were purchased from Aldrich and used as received. Their number-average molecular weights are listed in Table 1. The polydispersities were 1.1 or less. A cyclic PS (poly-

Table 1. Neat Polystyrene Data

	M_n (g/mol)	$\log \tau_0$ (s)	B (K)	T_0 (K)	T_g (K)	m	$E_a (T_g)$ (kJ/mol)
PS0.7k	739	−15.55	2450	210	271	79	408
PS3k	3,420	−15.59	2110	291	343	116	760
PS18k	18,040	−15.68	1990	315	364	131	915
PS104k	104,800	−13.73	1530	327	369	137	971
Cyclic PS[a]	4,360	−17.15	2119	323	370.7	148	1,050

[a]The data are from Santangello et al.[34]

dispersity $= 1.06$) was obtained from T. Chang and J. Roovers. Details of its preparation can be found elsewhere.[43] Various mixtures were prepared by dissolution in toluene followed by drying *in vacuo* at 130 °C. Test specimens were molded at 135 °C. Dynamic mechanical measurements were conducted isothermally at temperatures just above the T_g using a Rheometrics Dynamic Analyzer RDAII (maximum torque $= 2000$ g cm). A parallel plate geometry was employed with plate diameters of 5 mm and gaps between 1.0 and 1.5 mm. Oscillatory frequencies ranged from 0.001 to 40 rad/s at strains in the range of 0.05–0.3%. A nitrogen purge was applied during the measurements.

RESULTS

Figure 1 displays the peak in the loss modulus (G''), which is associated with segmental relaxation of two neat PSs and their 50/50 (w/w) blend. The spectra were normalized by the maximum in G'' and shifted to superimpose the peaks. There are three notable features in the data.

The first feature is that the shapes of the loss peak are the same for the two neat components, despite their large difference in molecular weight (corresponding to 8 and 1060 repeat units per chain). This invariance in the breadth of the segmental relaxation function to the molecular weight, seen previously for PS,[24,27] is noteworthy. Included in Figure 1 is the fit of the one-sided transform of the Kohlrausch–Williams–Watts function[44]

$$G(t) = G_0 \exp[-(t/\tau_k)^\beta]. \qquad (3)$$

in which G_0 is the glassy modulus, τ_K is a relaxation time, and the exponent $\beta = 0.46$. This is close to the value obtained for the dielectric α peak in PS, which is $\beta = 0.44$.[27]

The second feature is that the loss peak for the blend is substantially broader than for the neat components. This is a well-known consequence of the distribution of local environments engendered by concentration fluctuations. Local regions rich in the higher (lower) T_g component will contribute primarily toward the lower (higher) frequencies.

Table 2. Polystyrene Blend Data

		M_n (kg/mol)	$\log \tau_0$ (s)	B (K)	T_0 (K)	T_g (K)	m
50% PS0.7k	50% PS3k	1.22	−13.76	1990	211	285	82
50% PS0.7k	50% PS18k	1.42	−15.14	2540	235	300	80
50% PS0.7k	50% PS104	1.47	−16.03	2960	229	301	76
5% PS0.7k	95% PS104	13.0	−13.03	1590	313	359	117
50% PS3k	50% PS18k	5.75	−15.61	2200	293	347	112
50% PS3k	50% PS104k	6.62	−16.89	2550	293	351	113
50% PS3k	50% cyclic PS	6.62[a]	−13.66	1770	303	352	112

[a]For the M_n of cyclic PS we use 100 kg/mol (rather than the actual molecular weight), because the chain end concentration is the relevant quantity.
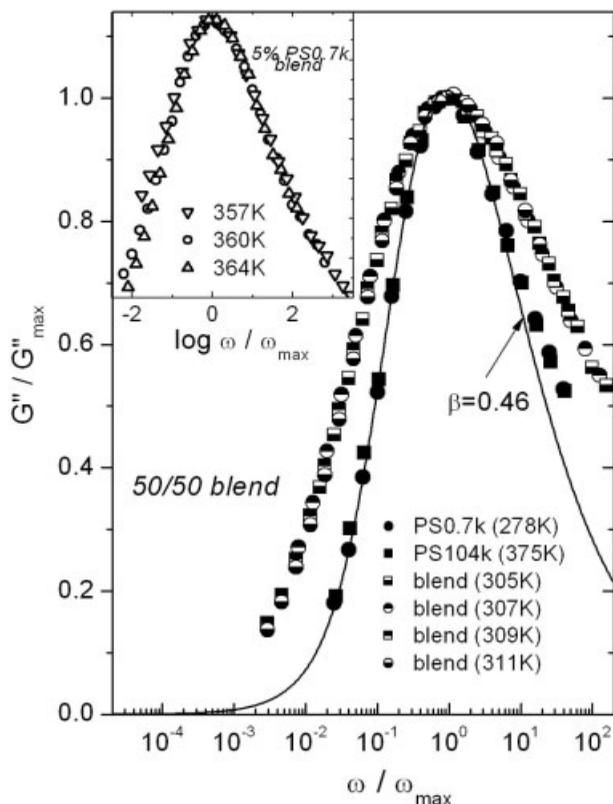
Figure 1. Segmental relaxation peaks in the loss modulus for the neat PS0.7k and PS104k and their 50/50 (w/w) blend at various temperatures. The peaks are vertically and horizontally scaled to superimpose the maxima. The actual ω_{max} (rad/s) = 0.993 and 0.942 for the PS0.7k and PS104k, respectively; for the blend ω_{max} = 0.0993 (303 K), 0.314 (307 K), 0.848 (309 K), and 2.14 (311 K). The height of the loss peak for the blend changes less than 2% over this 6° span. (—) The best fit to eq 3. (inset) The segmental relaxation peak for 5 wt % PS0.7k with PS104k. For this composition there is some slight broadening toward lower frequencies with decreasing temperature.

Consequently, this broadening is often asymmetric, being more prominent on the low frequency side.[45–47] The asymmetry is present in Figure 1, although the effect is subtle.

The third feature is that time–temperature superpositioning is valid for the loss peak of the blend. This is contrary to the usual behavior for local segmental relaxation in polymer blends.[48] Note that this thermorheological simplicity is obtained only after correction for the systematic change in the relaxation strength with temperature (1.8% decrease from 305 to 311 K). In addition, this superpositioning is only obtained for the segmental relaxation peaks. Extending to lower

frequencies, where chain modes begin to contribute to the mechanical response, the well-known breakdown of time–temperature superpositioning in the softening zone is observed.[49,50] In the inset to Figure 1 we show three spectra for the same components in a blend of 5% PS0.7k. For this composition there is some slight broadening toward lower frequencies with decreasing temperature.

The segmental relaxation times, defined from the maximum in the loss modulus, $\tau = 1/\omega_{max}$,[51] are shown in Figure 2 for the four neat PSs and for three blends of the lowest M_n sample (PS0.7k) with an equal weight of each of the other three materials. Figure 3 contains similar results for 50/50 blends of PS3k with high molecular weight PS. In all cases, the relaxation times do not fall midway between τ for the neat components, but rather are strongly weighted toward the lower molecular weight PS (i.e., toward lower temperatures). Also included in Figure 2 are the data for 5% PS0.7k with 95% PS104k. All these relaxation times were fit to the Vogel–Fulcher–Tamann–Hesse equation,[52]

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \qquad (4)$$

in which τ_0, B, and T_0 are constants, the latter identified with the Kauzmann temperature. The values of the fit parameters are listed in Table 1.
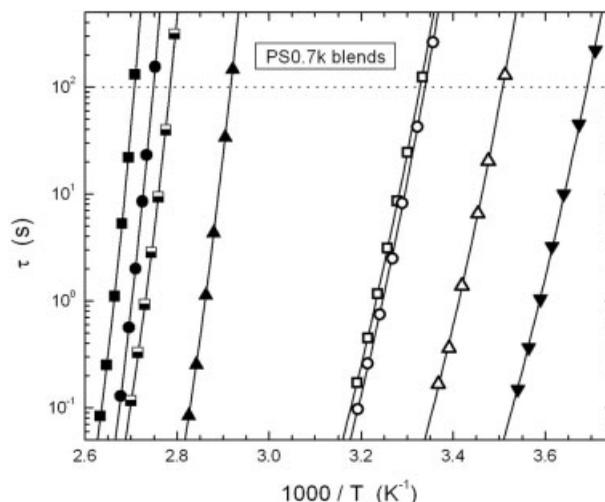

Figure 2. The segmental relaxation times for neat polystyrenes (▼) PS0.7k, (▲) PS3k, (●) PS18k, and (■) PS104k; 50/50 blends of PS0.7k with (△) PS3k, (○) PS18k, and (□) PS104k; and a blend of 5% PS0.7k with (◨) PS104k.
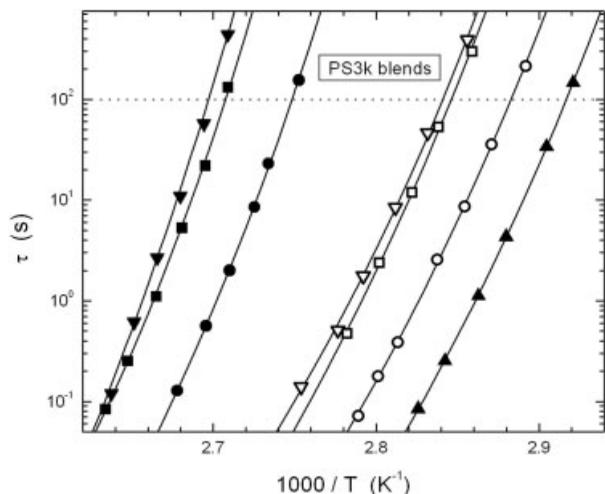
Figure 3. The segmental relaxation times for neat polystyrenes (▲) PS3k, (●) PS18k, and (■) PS104k; (▼) cyclic PS; and 50/50 blends of PS3k with (○) PS18k, (□) PS104k, and (▽) cyclic PS.

Using eq 4, we can interpolate the data in Figure 2 to determine the temperature at which τ = 100 s. This characteristic temperature is taken to be the T_g. Support for this identification comes from experiments at high pressure, in which an isochronally defined glass-transition temperature is found to remain equal to other experimental determinations of T_g values over broad ranges of pressure.[53,54] The value of T_g, of course, varies with pressure.

In Figure 4 these T_g values are inversely plotted versus the reciprocal of the number-average molecular weight, which yields a linear plot per eq 2. The figure also shows earlier results on similar PS samples.[34] The fit of all data, including both neat PS and the blends, yields $T_{g,\infty} = 366 \pm 3$ K and $k_{UK} = 0.76 \pm 0.03$ g/mol. The asymptotic value for the mechanical data is a couple degrees lower than obtained via calorimetry: $T_{g,\infty} = 374$ K.[24,27]

Because the Arrhenius plots in Figures 2 and 3 are nonlinear, we quantify the temperature dependence of the segmental relaxation times by calculating the fragility, with the results also
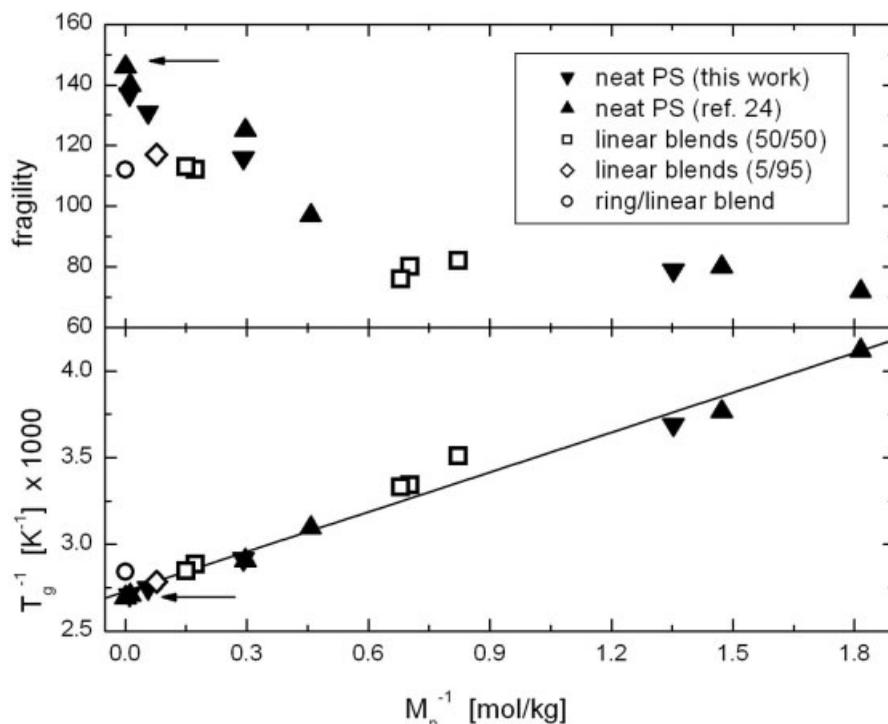

Figure 4. (upper panel) The fragility versus the inverse of the number-average molecular weight (M_n). (lower panel) The temperatures at which τ = 100 s for neat PS and blends, (—) plotted according to the form of eq 2. For blends containing cyclic PS, the M_n of the ring was taken to be 10^5 g/mol. The horizontal arrows indicate the values for the cyclic PS (from Santangelo et al.[34]).

shown in Figure 4 as a function of M_n^{-1}. Neat PS exhibits the systematic increase of m with molecular weights seen previously.[24,26,27] It is more interesting that the blends show the same behavior; in fact, the data points for the neat components and the blends are indistinguishable. With respect to the T_g and fragility, the cyclic PS in blends behaves exactly like PS with a high M_n value.

DISCUSSION

The neat components of the blend in Figure 1 have T_g values that differ by almost 100 °C. Given this large difference, we expect that local environments enriched in the lower M_n component will have more mobility, thereby contributing to the mechanical response at higher frequencies; conversely, local environments in which the higher M_n component predominates will influence the segmental dynamics at lower frequencies. It is this dynamic heterogeneity that gives rise to the broadening of the loss peak for the blend in Figure 1, in comparison to the G'' of the neat polymers. We have previously shown how this local mobility is reflected in the degree of intermolecular cooperativity of these local environments, with stronger intermolecular cooperativity associated with a broader relaxation function.[55,56] Indeed, there is a suggestion of extra broadening toward the low frequency side of the blend peak in Figure 1. For the dilute blend of PS0.7k, which has a more nearly equal molar composition, this asymmetric broadening is more evident (Fig. 1, inset). In such a composition, regions enriched in the higher T_g component are more abundant. Contributing at longer times, they give rise to the asymmetric broadening on the low frequency side of the peak.

Cooperativity also engenders a stronger temperature dependence of the relaxation times, which is expected to cause a breakdown of time–temperature superpositioning in blends. The thermorheological simplicity seen in Figure 1 for the 50/50 (w/w) mixtures indicates that the effect is weak for bidisperse PS blends. Note that the respective relaxation functions of the components are the same (Fig. 1), suggesting equivalent degrees of intermolecular cooperativity in their neat states. The T_g effect still remains, however, as manifested in the thermorheological complexity of the 5/95 (w/w) blend (Fig. 1, inset).

Usually, polymers exhibit the same fragility when their relaxation functions have the same breadth.[55] However, this correlation is not universal[29,30] and PS is evidently one such exception: the increasing fragility with increasing molecular weight (Fig. 4) is not accompanied by any broadening of the segmental relaxation function (Fig. 1). Moreover, the conclusion that τ for higher molecular weight PS exhibits a stronger temperature dependence does not rely on the use of fragility to characterize $\tau(T)$. The slope of the Arrhenius curves varies by about 30% over the temperature range in Figure 2, so that, strictly speaking, the activation energy is undefined. This is especially true near the T_g, where the liquid structure, including the intermolecular potential barriers, change with the temperature. However, we can compare the apparent activation energies (E_a) at T_g, which are calculated from the fragility as $E_a = RT_g m/\log e$. The results (Table 1) reinforce the idea that the temperature dependence is dependent on the molecular weight, notwithstanding the invariance of the peak breadths.

As noted above, the relaxation curves for the 50/50 blends in Figures 2 and 3 do not fall intermediately between the curves for the neat components. Such behavior is quite general for polymer blends. In fact, there are cases in which the relaxation times of blends are actually longer[57,58] or shorter[59–61] than τ for either of the neat components. As shown in Figure 4, however, the behavior of the bidisperse blends can be interpreted in terms of the dominant effect of chain ends. For both the relaxation times per se, as reflected in the respective T_g values and in the T_g-normalized temperature dependence of τ, the behavior is governed primarily by the concentration of chain ends. Of course, for the linear PS herein, the chain end concentration can be quantified using the M_n.

The T_g coefficient in eq 2 determined from the data in Figure 3 ($k_{UK} = 0.76$) is substantially larger than the value of 0.52 reported by Ueberreiter and Kanig.[9] However, their experiments utilized PS chains containing as few as two monomer units and the analysis strongly weights the smaller molecules. This is problematic because the end groups are quite different chemically than the PS repeat units; the dimer, for example, cannot be considered to be PS.

Our finding that the fragility is governed by the concentration of chain ends is consistent with our results for the blend of PS3k with low M_n (4.36 kg/mol) cyclic PS. The relaxation times of

this blend are as long as τ_α for PS3k blended with the highest molecular weight sample (M_n = 104.k kg/mol). Likewise, the T_g value is highest for the PS3k/ring blend compared to any other blend with the PS3k polymer. These results reinforce the findings of our earlier work in which the fragility of low molecular weight cyclic PS was equal to the high molecular weight limiting value of m.

CONCLUSIONS

The segmental relaxation properties of PS, including the magnitude of the relaxation times, the glass-transition temperature, and the fragility, are governed by the chain end concentration. Even in bidisperse blends, having very nonuniform concentrations of the two components, and for blends of linear and cyclic PS, the dominant influence is the average concentration of chain ends. We also observed the previously reported anomaly of increasing fragility with increasing molecular weight, despite an invariance of the shape of the segmental relaxation function to the chain length.

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