

Molecular Weight Dependence of Polystyrene Segmental Dynamics in Dilute Blends with Poly(vinyl methyl ether)

LIANG ZHANG, T. R. LUTZ,* JUNSHU ZHAO, M. D. EDIGER

Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

Received 9 January 2007; revised 19 April 2007; accepted 21 April 2007

DOI: 10.1002/polb.21232

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The segmental dynamics of backbone-deuterated polystyrenes (d_3 PS) with varying molecular weights (1.7–67 kg/mol) have been measured in blends with poly(vinyl methyl ether) (PVME). ^2H NMR T_1 values at 15 and 77 MHz are reported for the pure d_3 PS and for the dilute d_3 PS component in PVME matrices. The temperature shift that is needed to superpose the NMR T_1 data for the pure d_3 PS and the d_3 PS as a dilute component in the blend ranges from 45 to 70 K. In the framework of Lodge/McLeish model, the self-concentration value for d_3 PS in these dilute blends with PVME is found to be independent of molecular weight. We thus establish for this system that the substantial influence of molecular weight on the blend segmental dynamics can be explained by homopolymer T_g differences. ©2007 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 45: 2252–2262, 2007

Keywords: blends; polystyrene; relaxation

INTRODUCTION

A great deal of recent attention has focused upon dynamics in miscible polymer blends. Although these systems form a single thermodynamic phase that is mixed on a molecular level, there is strong evidence that the individual components in the blend do not in general have similar relaxation times.^{1–20} In the blend of polyisoprene and polyvinylethylene, for example, the segmental relaxation times of the two components can differ by up to four orders of magnitude, if the temperature is low and the blend is rich in polyvinylethylene.⁶ Even though miscible blends typically show a single glass transition temperature T_g as measured by calorimetry, the transition is broad and consistent with the distinct component dynamics observed in dielectric relaxation, NMR,

and other experiments.^{7,21} Each component in the blend can be assigned its own effective glass transition temperature $T_{g,\text{eff}}$.^{3,7} The overall calorimetry signal is then interpreted as a combination of two broad processes occurring at different temperatures. In a few cases, two separate calorimetric transitions have been observed in miscible blends.^{21–23}

For homopolymers, it is well understood that there are two conceptually distinct ways to change T_g while maintaining a pure homopolymer melt. Either the chemical structure of every repeat unit can be modified to form a different homopolymer, or the molecular weight can be altered without changing the structure of the repeat unit; for linear homopolymers, increasing molecular weight increases T_g up to an asymptotic value. These same two methods can be used to alter $T_{g,\text{eff}}$ for one component in a miscible polymer blend. In this article, we address whether or not these two ways of changing $T_{g,\text{eff}}$ are equivalent.

It is easiest to describe this issue in terms of a particular model. The Lodge-McLeish (LM) model, for example, in its most simple form (combined

*Present address: Stepan Company, 22 W. Frontage Road, Northfield, IL 60093.

Correspondence to: M. D. Ediger (E-mail: ediger@chem.wisc.edu)

Journal of Polymer Science: Part B: Polymer Physics, Vol. 45, 2252–2262 (2007)
©2007 Wiley Periodicals, Inc.

with the Fox equation), predicts $T_{g,\text{eff}}$ for a given component in a binary blend using four parameters: the blend composition ϕ , the glass transition temperatures of the two homopolymers, and the self-concentration ϕ_{self} for the component of interest.³ Although ϕ_{self} is calculated from a number of homopolymer properties, none of these vary significantly with molecular weight down to quite low molecular weights. Thus, this version of the LM model says that molecular weight per se is not an important parameter for blend segmental dynamics. In this context, molecular weight influences $T_{g,\text{eff}}$ only insofar as it changes the T_g of the homopolymers.

The effect of molecular weight on the segmental dynamics of miscible blends is also an important practical issue. Molecular weight has a strong influence on the viscoelastic properties of miscible blends.^{19,24} This influence is a combination of a topological effect (e.g., increasing entanglements) and the changes in local dynamics that occur with molecular weight. In addition, many experiments have been done on miscible blends in which at least one component is low enough in molecular weight that its T_g (as a homopolymer) is substantially less than the high molecular weight value.^{12,13,25–27} Often, this strategy has been utilized to achieve miscibility in systems that otherwise would phase separate. It would be useful to know if it is fair to compare these results with those obtained using high molecular weight blends. While it has generally been assumed that this is the case, we address this point explicitly here.

In this article, we report an NMR investigation of the segmental dynamics of backbone-deuterated polystyrenes ($d_3\text{PS}$) with varying molecular weights as pure melts and as a dilute component in blends with poly(vinyl methyl ether) (PVME). The PS/PVME system is chosen because of its miscibility over a wide range of molecular weights and the large T_g difference between the two homopolymers. This latter factor accentuates the degree to which the two components exhibit distinct segmental dynamics.² The PS/PVME system has been well characterized in other respects, including phase behavior,^{28,29} segmental dynamics,^{30–37} and terminal dynamics.^{32,38–42} The PS/PVME system shows LCST phase behavior^{28,29,43,44} and its dynamics are thermorheologically complex at both the segmental and terminal levels.³²

Here, we utilize $d_3\text{PS}$ with molecular weights of 2, 15, and 67 kg/mol. The T_g difference

between the PS and PVME components in our blends varies from 81 to 126 K, depending upon the PS molecular weight. Thus, in our study, the influence of molecular weight and chemical structure on the difference in T_g between the two components in the blend are nearly comparable. We report the segmental dynamics of the polystyrene component in blends that contain only 2% PS. As shown previously, this procedure investigates the properties of dilute chains that are essentially isolated from one another in a host matrix, and thus intermolecular concentration fluctuations have a negligible effect on our results.^{4,25,45}

We find that each of the three $d_3\text{PS}/\text{PVME}$ blend systems examined shows distinct segmental dynamics. The temperature shifts needed to describe the effect of blending upon the dilute $d_3\text{PS}$ component range from 45 to 70 K, depending upon the $d_3\text{PS}$ molecular weight. Using the LM model,³ we find that a single ϕ_{self} value can reasonably describe the segmental dynamics of $d_3\text{PS}$ in all three dilute PS/PVME blends. For this particular system, we can answer the questions posed above about the influence of molecular weight upon segmental dynamics in miscible blends. Within the context of the LM model, knowledge of the homopolymer T_g values is sufficient for understanding the component segmental dynamics even if these T_g values are substantially influenced by the low molecular weight of a blend component.

EXPERIMENTAL

Materials

Backbone deuterium enriched PS of three molecular weight were purchased from Polymer Source; $M_n = 1.7$ kg/mol ($d_3\text{PS}2\text{k}$), $M_n = 15$ kg/mol ($d_3\text{PS}15\text{k}$), and $M_n = 67$ kg/mol ($d_3\text{PS}67\text{k}$). PVME with $M_n = 48.5$ kg/mol was obtained from Scientific Polymer Products. Characterization information for all polymers is given in Table 1.

Table 1. Sample Characterization

Sample	M_n (g/mol)	M_w/M_n	T_g (K)
$d_3\text{PS}2\text{k}$	1,670	1.06	331
$d_3\text{PS}15\text{k}$	15,000	1.04	373
$d_3\text{PS}67\text{k}$	67,000	1.05	376
PVME	48,500	1.95	250

Sample Preparation

All the pure d_3 PS samples were prepared by loading 0.5 g of granular PS into 5-mm diameter NMR tubes. The tubes were then placed in a vacuum oven at room temperature for 24 h, then heated to $T_g - 20$ K for 4 h, and finally heated to $T_g + 50$ K for 2 h. This temperature program removed any residual solvent from the polymer and allowed the sample to flow into a continuous melt at the bottom of the NMR tube. The samples were then cooled to room temperature and sealed under vacuum.

The 2% d_3 PS2k/PVME blend was prepared by solvent casting dilute THF solutions (about 500 mg of total polymer in 50 mL solvent). The blend was stirred for 24 h to ensure complete mixing. After approximately 90% of the solvent was removed by blowing N_2 gas onto the solution surface, the solution was transferred to an NMR tube and the remaining solvent was removed under vacuum. As the viscosity increased with the removal of THF, the solution was coated as a thin film onto the wall of the NMR tube and held under vacuum for at least 24 h to ensure complete removal of solvent. Finally the blend was heated and allowed to flow to the bottom of the NMR tube. The sample was then sealed under vacuum.

A different method was used to prepare the 2% d_3 PS15k/PVME and 2% d_3 PS67k/PVME blends since they are more viscous and do not flow easily upon heating. Approximately 500 mg of total polymer was dissolved in 50 mL of THF and this solution was placed in a vial. Solvent was removed under vacuum at room temperature for 48 h, after which the samples were heated at 348 K for 24 h, and then 400 K for 3 h. Because the polymer blend film in the vial was thin (~ 1 mm), this procedure allowed complete removal of the solvent. The vial containing the blend was then submerged rapidly into liquid nitrogen. While taking care to keep the blend in the glassy state, the vial was broken and small pieces of the blend were carefully separated from the broken vial and transferred to an NMR tube. The blend bits were lightly pressed into the bottom of the NMR tube and placed under vacuum for 24 h. Next the samples were placed in the vacuum oven and heated at 400 K for about half an hour. Finally the NMR tubes were sealed under vacuum.

T_g and Miscibility

Differential scanning calorimetry measurements were carried out on a Netzsch 200 DSC. Four

successive heating and cooling cycles were run at a rate of 10 K/min over temperatures ranging from $T_g - 50$ K to $T_g + 50$ K. T_g is taken as the midpoint of the transition trace. Successive scans gave T_g values that agree to within 1 K and the average values are reported in Table 1.

We performed cloud point measurements to ensure that our NMR experiments were only conducted in the one phase region. Previous studies have shown that PS/PVME has a LCST phase diagram.^{28,29,43,44} Cloud points for d_3 PS67k/PVME blends are shown in Figure 1. The 2% d_3 PS67k/PVME blend utilized in our NMR experiments does not phase separate until the temperature reaches 428 K. We limited our experiments on this sample to lower temperatures. Based on this result, we expect that 2% blends of d_3 PS with lower molecular weights will remain in the single phase regime up to higher temperature. Consistent with this expectation, no cloud point was found for 2% d_3 PS2k/PVME or 2% d_3 PS15k/PVME blends up to 473 K, the limit of our NMR measurements. All the cloud point tests were carried out in a vacuum oven to avoid oxidization.

NMR Measurements

2H NMR spin-lattice relaxation times T_1 were measured by the standard inversion-recovery ($\pi - \tau - \pi/2$) pulse sequence, waiting more than

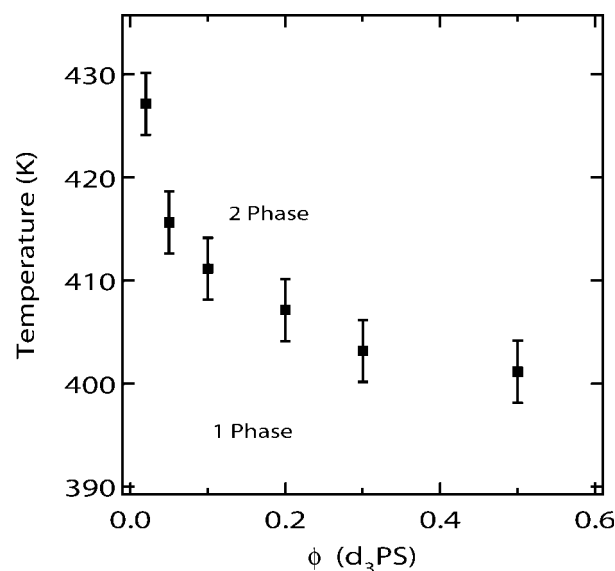


Figure 1. Cloud point measurements for d_3 PS67k/PVME blends.

10 times T_1 between the acquisition and the next pulse. T_1 is the time required for the magnetization to return to its equilibrium state and, as we discuss below, it is sensitive to segmental dynamics. The number of scans used for signal averaging varied from 128 to 1024, depending on the temperature. The data was processed with line broadening equal to one-tenth of the line width of the spectrum. All T_1 values presented in this article were calculated using peak area, based upon at least three trials. The uncertainty in T_1 is $\pm 5\%$. Peak areas are used rather than peak intensities since for low molecular weight samples the latter gives disproportionate influence to the dynamics near the chain ends.

All measurements were performed on a Varian Inova-500 NMR spectrometer (76.7 MHz) and a Bruker DMX NMR spectrometer (15.2 MHz). Temperature was controlled to ± 0.5 K and calibrated within ± 3 K using a combination of an ethylene glycol thermometer and melting point standards. All measurements were done in the one phase region. As a test for sample degradation, T_1 was reacquired at lower temperatures after exposure to high temperature. The latter results agreed with earlier measurements within experimental error, and thus we conclude that no significant sample degradation occurs in the temperature range of our measurements.

Data Interpretation

Electric quadrupole coupling is the dominant factor determining the rate of ^2H spin-lattice relaxation. The equation below^{46–48} is the description of the relationship between the spin-lattice relaxation time T_1 and the reorientation of a C-D bond.

$$\frac{1}{T_1} = \frac{3}{10} \pi^2 \left(\frac{e^2 q Q}{h} \right)^2 [J(\omega) + 4J(2\omega)] \quad (1)$$

Here $\omega/2\pi$ is the Larmor frequency and the quadrupole coupling constant $e^2 q Q/h$ is taken as 172 kHz for $d_3\text{PS}$ backbone deuterons.^{48–50} $J(\omega)$ is the spectral density function:

$$J(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} G(t) e^{-i\omega t} dt \quad (2)$$

$G(t)$ is the orientation autocorrelation function which describes the reorientation of a C-D inter-nuclear vector.

$$G(t) = \frac{3}{2} \langle \cos^2 \theta(t) \rangle - \frac{1}{2} \quad (3)$$

Here $\theta(t)$ is the angle of the C-D bond relative to its orientation at time $t = 0$.

As shown in eqs 1–3, the connection between the experimental observable T_1 and molecular motion is made through the orientation autocorrelation function $G(t)$ for a C-D bond vector. The modified Kohlrausch-Williams-Watts function is used to represent the autocorrelation function $G(t)$:

$$G(t) = a_{\text{lib}} e^{-t/\tau_{\text{lib}}} + (1 - a_{\text{lib}}) e^{-(t/\tau_{\text{seg}})^\beta} \quad (4)$$

This function indicates that C-D vector reorientation occurs through two mechanisms: librational and segmental motions. a_{lib} and τ_{lib} characterize the amplitude and relaxation time for librational motion. τ_{lib} was set to 1 ps since our fitting analysis is insensitive to its precise value. τ_{seg} and β describe a characteristic segmental relaxation time as well as its distribution. We assume τ_{seg} follows a VTF dependence:^{51,52}

$$\log \left(\frac{\tau_{\text{seg}}}{\tau_\infty} \right) = \frac{B}{T - T_0} \quad (5)$$

Here τ_∞ , B , and T_0 are constants for a given component in a particular blend. The correlation time for segmental dynamics $\tau_{\text{seg,c}}$ is the time integral of the segmental portion of the correlation function:

$$\tau_{\text{seg,c}} = \frac{\tau_{\text{seg}}}{\beta} \Gamma \left(\frac{1}{\beta} \right) \quad (6)$$

We report our results as $\tau_{\text{seg,c}}$ rather than τ_{seg} since the former quantity is determined with higher precision.

RESULTS

NMR Spin-Lattice Relaxation Times

^2H T_1 values for pure low molecular weight polystyrene ($d_3\text{PS}2\text{k}$) and for this polymer as a dilute component in a PS/PVME blend are presented in Figure 2. The upper and lower curves are measured at 76.7 and 15.2 MHz, respectively. At each field, the temperature where the T_1 minimum occurs for the $d_3\text{PS}2\text{k}$ is shifted about 45 K to lower temperature after it has been blended with PVME. Since the T_1 minimum approximately

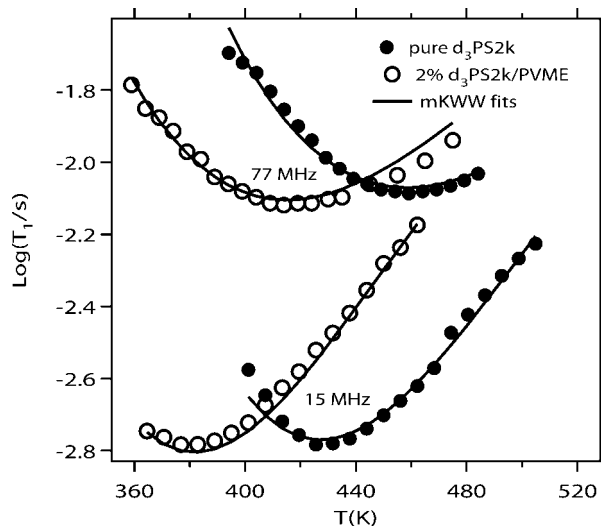


Figure 2. NMR T_1 values of pure d_3 PS2k (solid circles) and 2% d_3 PS2k (open circles) blended with PVME at 15.2 and 76.7 MHz. Solid lines are mKWW fits obtained by simultaneously fitting all the data for a given blend.

indicates the temperature at which the segmental dynamics occur on a 1 ns timescale, this indicates that the segmental dynamics of PS become faster when they are surrounded by PVME segments as opposed to PS segments. Note that a 45 K shift is much less than the ΔT_g of 81 K for this blend. Since the dynamics of the PVME component in the blend should be very similar to pure PVME dynamics, this result is an indication of distinct segmental dynamics for the two components in this blend. If the PS dynamics were slaved to the dynamics of the PVME matrix, a temperature shift of ~ 81 K would have appeared in Figure 2.

Figures 3 and 4 are analogous to Figure 2 and they show the results for dilute blends of higher molecular weight d_3 PS chains with the same PVME sample used in the experiments shown in Figure 2. Because of the temperature limitation of our NMR probe, we could not measure the T_1 minimum for pure d_3 PS15k and d_3 PS67k samples at the higher field. However, the data acquired at 15 MHz does not have this limitation. The temperature shifts upon blending for these samples is larger than that shown in Figure 2; this is expected since ΔT_g has increased. As was the case for Figure 2, the temperature shifts in Figures 3 and 4 are considerably smaller than the ΔT_g values for the blends.

We note that the pure PS data in Figures 2–4 is consistent with our expectations based upon

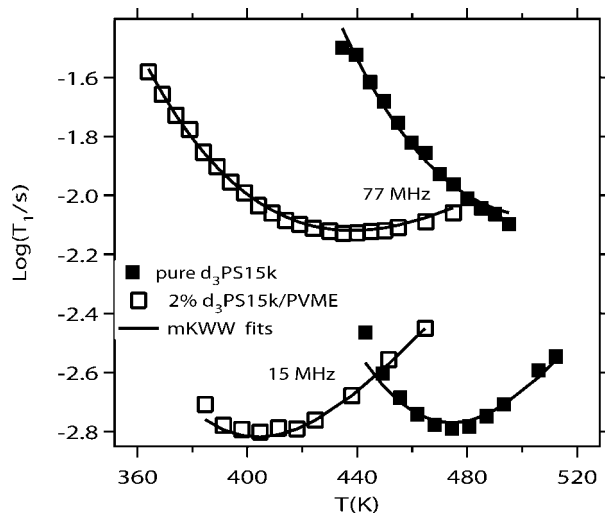


Figure 3. NMR T_1 values of pure d_3 PS15k (solid squares) and 2% d_3 PS15k (open squares) blended with PVME at 15.2 and 76.7 MHz. Solid lines are mKWW fits obtained by simultaneously fitting all the data for a given blend.

the T_g values for these samples. The T_1 minimum of the pure PS moves to higher temperature as the molecular weight of PS increases, which indicates that the segmental dynamics of PS become slower with increasing molecular weight. The temperature difference between the T_1 minima of the pure PS samples is equal to the T_g difference (within a few K) as reported in previous work.⁵³

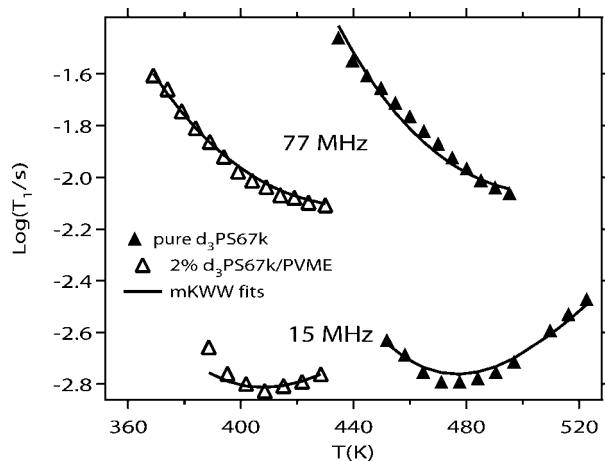


Figure 4. NMR T_1 values of pure d_3 PS67k (solid triangles) and 2% d_3 PS67k (open triangles) blended with PVME at 15.2 and 76.7 MHz. Solid lines are mKWW fits obtained by simultaneously fitting all the data for a given blend.

Table 2. Fitting Parameters for d_3 PS Segmental Dynamics

Sample	B (K) ^a	T_0 (K) ^b	τ (ps)	a_{lib} ^c	β ^c
d_3 PS2k	700	265	0.23	0.12	0.45
d_3 PS15k	700	310	0.27	0.21	0.50
d_3 PS67k	700	313	0.26	0.19	0.48
2% d_3 PS2k/PVME	700	215	0.31	0.14	0.50
2% d_3 PS15k/PVME	700	235	0.35	0.06	0.47
2% d_3 PS67k/PVME	700	240	0.33	0.04	0.46

^a B constrained to 700 K.^b Uncertainty is 15 K.^c Uncertainty is 0.07.

Segmental Correlation Times

To extract the maximum information from the NMR T_1 values, we fit the experimental results to the motional model described in the Experimental Methods section. In brief, we used a modified Kohlrausch-Williams-Watts function (eq 4) to describe the orientation autocorrelation function of a C-D bond at a particular temperature. The segmental correlation time $\tau_{\text{seg},c}$ is a characteristic decay time for this function. $\tau_{\text{seg},c}$ as function of temperature is obtained by this procedure, with the assumption that the temperature dependence can be described by the Vogel-Tammann-Fulcher equation (eq 5).

Figures 2–4 show solid lines indicating the fits obtained by this procedure. In every case, all the T_1 data at both frequencies for a given sample are simultaneously fit using five fitting parameters: a_{lib} , τ_{∞} , β , B , and T_0 . As shown in the figures, the quality of the fits is quite good. The fitting parameters obtained are presented in Table 2.

The segmental correlation times for PS segments in the pure melts and in each blend as a function of temperature are shown in Figure 5; these were calculated using eq 6 and the parameters in Table 2. Representative error bars for the calculated correlation times are shown. Figure 5 shows that the segmental dynamics of PS are speeded up by the presence of PVME segments, especially for d_3 PS15k and d_3 PS67k, and this effect is more pronounced at lower temperature. For example, for d_3 PS15k at 430 K, the segmental relaxation time is about 100 times faster upon blending with PVME.

The dependence of the correlation time upon temperature is almost identical for the three pure PS samples over the temperature range of this NMR study. If we shift the curves by ΔT_g , an

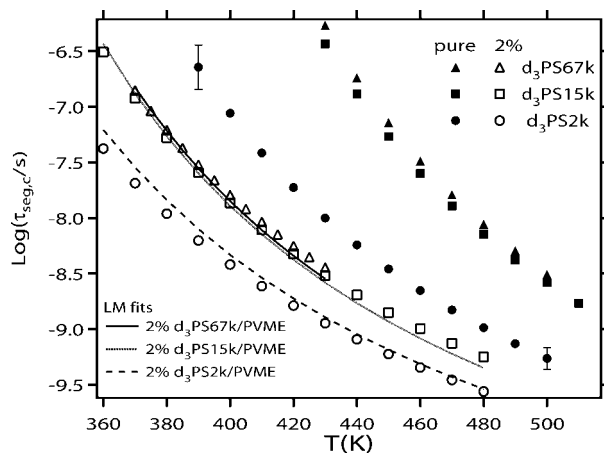


Figure 5. Segmental correlation times for pure d_3 PS of three molecular weights as pure melts and as 2% blends with PVME. The solid symbols are the calculated correlation times for pure d_3 PS melts while the open symbols are the calculated correlation times for d_3 PS as a dilute component in the blends. Correlation times are calculated using the fit parameters in Table 2. The lines are the fits of the LM model to the blend segmental correlation times with $\phi_{\text{self}} = 0.52$.

excellent master curve is obtained, as shown in Figure 6. This result supports the view that the segmental dynamics of PS melts of differing molecular weights are identical if the temperature scale is shifted to account for the differing T_g values,⁵³ at least for temperatures well above T_g .

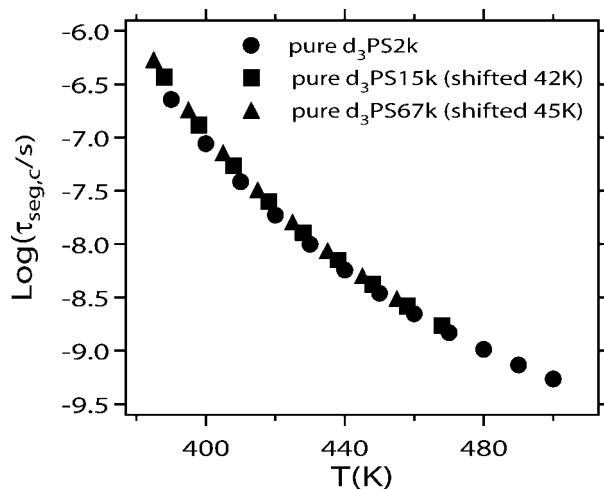


Figure 6. Segmental correlation times for the three pure d_3 PS samples. The correlation times for the higher molecular weight samples have been shifted by an amount ΔT_g as indicated. To a good approximation, these three samples show identical segmental dynamics after correcting the temperature for T_g differences.

Our results show that this applies for molecular weights ranging from 1700 to 67,000 g/mol.

A few details about the fitting procedure need to be stated explicitly. Because of relatively small range of correlation times probed by the NMR measurements, the VTF parameters (B and T_0) are highly correlated with each other. Based on preliminary fits, B was constrained to be 700 K for all blends studied. Given this constraint, T_0 is accurate within 15 K, while a_{lib} and β both have a typical uncertainty of 0.07. As a check, we also fit all the data without any constraints on the five parameters. This method yielded essentially the same $\tau_{seg,c}$ values as those shown in Figure 5. At no point, do these two fitting procedures yield $\tau_{seg,c}$ values that differ by more than the error bars shown.

DISCUSSION

Effect of Molecular Weight on Blend Dynamics

As discussed in the introduction, we wish to consider the effect of molecular weight on the segmental dynamics of miscible blends in which the repeat unit structure of the blend components is unchanged. Before comparing our data to model predictions, we directly compare the experimental data for the blend systems with the data for the corresponding pure polystyrene melts. In Fig-

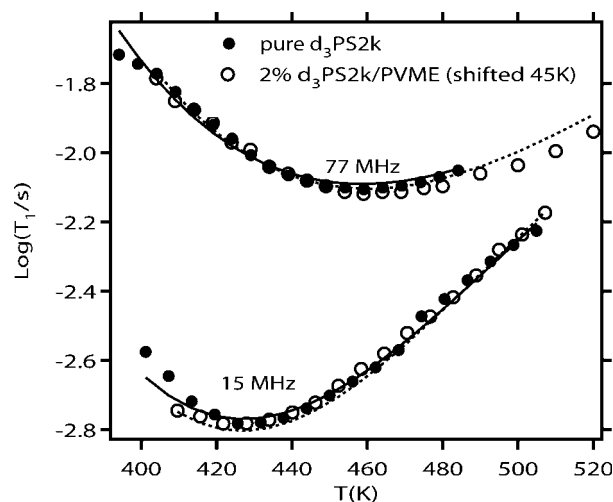


Figure 7. Superposition of T_1 data for d_3 PS2k in the homopolymer and 2% d_3 PS2k/PVME blends. A small vertical shift has been applied to the 77 MHz data. The pure d_3 PS2k data is plotted at the experimental temperature while the blend data is shifted by amount shown. The lines show mKWW fits from Figure 2.

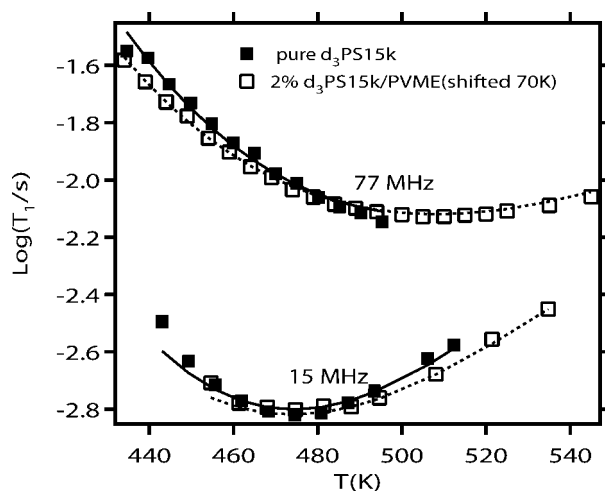


Figure 8. Superposition of T_1 data for d_3 PS15k in the homopolymer and 2% d_3 PS15k/PVME blends. A small vertical shift has been applied to the data taken at 77 MHz.

ure 7, we show that the NMR T_1 data for the d_3 PS2k sample in the blend is very similar to the data for a pure melt of d_3 PS2k if a temperature shift of 45 K is uniformly applied to the blend data at each field. This implies that the effect of blending in this sample to a first approximation is to lower the effective T_g ($T_{g,eff}$) of the PS chains by 45 K without changing other aspects of the dynamics. Similar statements may be made about the higher molecular weight PS samples as shown in Figures 8 and 9. Here, the shift in $T_{g,eff}$ for the PS chains is 70 K in both cases. These

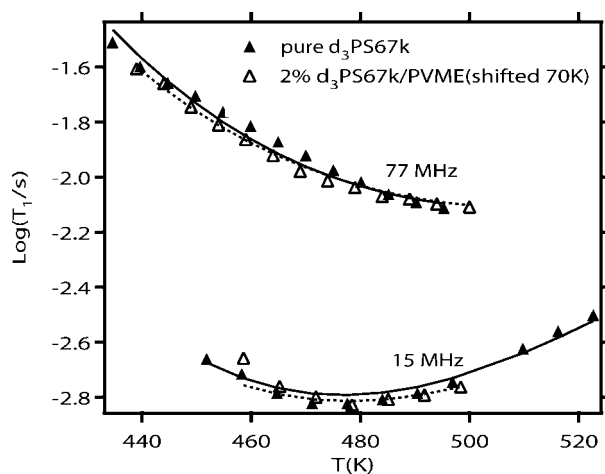


Figure 9. Superposition of T_1 data for d_3 PS67k in the homopolymer and as a dilute component in PS/PVME blends. Small vertical shifts have been applied to the data.

same temperature shifts are obtained by shifting the correlation times shown in Figure 5. In constructing Figures 7–9, we have made small vertical shifts in the data (less than 0.05) to achieve the best superposition.

Based upon these comparisons, we can make two statements about these blended systems. First, the dilute chains are clearly not slaved to the dynamics of the host PVME matrix, since in all cases $\Delta T_{g,\text{eff}}$ (45–70 K) is considerably less than the ΔT_g between the homopolymers (81–120 K). Second, even though the dilute PS chains are essentially completely surrounded by PVME chains, and isolated from each other, the molecular weight of the dilute chains does influence their dynamics. As shown in Figure 5, at a given temperature, the dilute low molecular weight PS chains have $T_{g,\text{eff}}$ about 25 K lower than the dilute higher molecular weight chains. However, the influence of molecular weight on the dilute chain's dynamics is not simply related to the T_g difference between the PS chains (~ 45 K).

Fits to the Lodge-McLeish Model

Next, we consider the extent to which the quantitative features of the data can be explained by the Lodge-McLeish (LM) model.³ This model has been reasonably successful in describing blend dynamics in a wide range of systems, including dilute blends. As described in the introduction, molecular weight does not explicitly enter the LM model, except that the self-concentration calculation would be inaccurate for extremely short chains. This article is the first direct test of the ability of this model to describe blend dynamics when large changes in the homopolymer T_g values are caused by molecular weight.

The LM model assumes that the relaxation rate of a given polymer segment in a blend is determined by the local composition in the region surrounding the segment. In this model, the Kuhn length l_k is assumed to be the relevant length scale for defining the local composition. Because of chain connectivity, the concentration of a particular blend component (within the volume $V = l_k^3$) surrounding a segment of this component is larger than the bulk concentration. The effective local concentration ϕ_{eff} is calculated as:

$$\phi_{\text{eff}} = \phi_{\text{self}} + (1 - \phi_{\text{self}})\phi \quad (7)$$

ϕ_{self} is estimated as the volume fraction occupied by one Kuhn length of the polymer inside the

volume $V = l_k^3$.

$$\phi_{\text{self}} = \frac{C_\infty M_0}{k\rho N_{\text{AV}}V} \quad (8)$$

Here C_∞ is the characteristic ratio, M_0 is the repeat unit molar mass, k is the number of backbone bonds per repeat unit, ρ is the density, and N_{AV} is Avogadro's number.

This model associates ϕ_{eff} for each component with a local glass transition temperature $T_{g,\text{eff}}(\phi) = T_g(\phi_{\text{eff}})$. The LM model is sometimes combined with Fox equation, in which case $T_g(\phi_{\text{eff}})$ can be calculated as

$$\frac{1}{T_g(\phi_{\text{eff}})} = \frac{\phi_{\text{eff}}}{T_{g,A}} + \frac{(1 - \phi_{\text{eff}})}{T_{g,B}} \quad (9)$$

The segmental dynamics of a particular component in the blend can be predicted by correlating changes in $T_{g,\text{eff}}$ with changes in T_0 ,

$$T_{0,i}(\phi) = T_{0,i} + [T_{g,i}(\phi) - T_{g,i}] \quad (10)$$

while assuming that the remaining VTF parameters (B , τ_∞) do not change with blending.

Figure 5 shows that all d_3 PS segmental correlation times in dilute PS/PVME blends can be reasonably fit by the LM model using a single value for the self-concentration of 0.52. The uncertainty in this determination of the self concentration value is 0.05, as estimated by the point where the deviation from the fitting is comparable to the experimental uncertainty. The self-concentration can also be estimated from the temperature shifts required to superpose the raw data. This procedure yields values of 0.51, 0.52, and 0.54, respectively, for the data from Figures 7–9. These values of the self-concentration are reasonably consistent with a previously published value for PS in PVME (0.46 ± 0.05). All of these values are considerably larger than the self-concentration of 0.27 that is calculated from eq 8.

In the introduction we asked whether molecular weight has a unique influence on the component segmental dynamics in a miscible polymer blend. Within the context of the LM model, the answer is “no”. The effects of molecular weight can be accounted for through the change in the homopolymer T_g value. Clearly this conclusion is limited to the temperature range well above T_g that we have studied. We anticipate that the data presented here will also be useful to testing other models of blend dynamics.

In our implementation of the LM model, we have used the Fox equation (eq 9) to estimate the blend T_g . For some molecular weight combinations in PS/PVME blends, it has been shown that the Fox equation slightly overestimates the blend T_g .⁵⁴ These effects are small enough that use of the experimental data, rather than the Fox equation, would not result in a significantly different value of the self-concentration values, given our error bars.

Comparison with Other Work

Based upon the discussion earlier, we find that a single value of self-concentration can describe the dynamics of dilute PS in PS/PVME blends even though T_g values of the PS homopolymers have been varied by 45 K. This is consistent with the idea that segmental dynamics in miscible blends are only influenced by molecular weight indirectly, through the homopolymer T_g . In this section, we examine this finding in light of previously reported work.

Lutz et al.²⁵ measured the segmental dynamics of dilute polyisoprene chains (900 g/mol) in polystyrene matrices with two different molecular weights (1900 and 11,000 g/mol). Although the matrix T_g values differ by 20 K, they reported that a single value of self concentration (0.22) could be used in the LM model to describe the segmental dynamics of the dilute polyisoprene chains in both matrices. While this conclusion is consistent with the work reported here, the results of ref. 25 were not a very sensitive test of this conclusion, since $T_{g,\text{eff}}$ of the dilute polyisoprene chains changed little with the matrix molecular weight. In contrast, in this study the $T_{g,\text{eff}}$ of the dilute PS chains change by 25 K as molecular weight is varied.

Hirose et al.⁵⁵ studied the component dynamics of miscible polyisoprene/polyvinylethylene (PI/PVE) blends. They measured PI dynamics in PI/PVE (75/25) blends composed of PIs with three different molecular weights (17,000–115,000 g/mol), and estimated the relevant length scale for the segmental relaxation dynamics. They found a single relevant length scale (0.9 ± 0.06 nm) for PI segmental dynamics in the three blends, which is consistent with a single self concentration value in LM model. Similar to the work presented here, they varied the molecular weight of the minor component while keeping the matrix chains unchanged. However, the T_g range for the

PI in their study is quite small, just a few degrees, so the work reported here is a considerable extension of this approach.

In a study of the composition and temperature dependence of terminal and segmental dynamics in PI/PVE blends, Haley et al.⁹ investigated both low molecular weight blends and high molecular weight blends of both components. The molecular weights (and T_g values) of both components were changed together. Because of this, and because the ΔT_g values for PI or PVE were considerably smaller than in the present work (less than 15 K), ref. 9 can be considered to be consistent with the conclusion reached here without being a critical test of this view.

Several investigations have considered the segmental dynamics of bidisperse polystyrene chains.²⁶ This special case of a miscible blend would in principle provide a critical test of the role of molecular weight on blend dynamics. So far, such studies have not resolved the dynamics of each component in the blend, which would be a necessary condition for addressing the role of molecular weight on component dynamics.

Final Comments on Low Molecular Weight Blends

In this article, we report that molecular weight influences the dynamics of a dilute component in a miscible blend only though the molecular weight dependent T_g change. We have covered a molecular weight range from 1700 to 67,000 g/mol in the work described here. It seems safe to extrapolate this result to infinite molecular weight, as long as phase separation does not occur. On the other hand, we anticipate a significant change as the molecular weight is dropped below 1700 g/mol. We have argued previously that PS chains of about 1700 g/mol are just long enough that the self-concentration concept can be applied without needing to correct for chain end effects.⁴⁵

Clearly the self-concentration concept needs serious re-consideration when only one or a few repeat units are present on a chain. In the limit of a single repeat unit (i.e. a solvent molecule), it would not seem appropriate to use a self-concentration description. Consistent with this view, we have recently shown that dilute small molecules dispersed in a polymer matrix can be slaved to the matrix relaxation in a manner that is qualitatively different than the behavior of an isolated polymer chain.⁵⁶

CONCLUSIONS

We have investigated the nanosecond to microsecond segmental dynamics of d_3 PS of various molecular weights as a dilute component in blends with PVME. The molecular weights of the polystyrene chains ranged from 1.7–67 kg/mol and the pure polystyrene T_g values varied by 45 K. Within the framework of the LM model, a single self concentration value can reasonably describe the segmental dynamics of d_3 PS with different molecular weights in dilute PS/PVME blends. For this system, the molecular weight influences segmental dynamics in the blend in manner that can be understood by considering only the change in T_g with molecular weight.

The authors thank the National Science Foundation (DMR-0355470) for support of this work.

REFERENCES AND NOTES

- Kim, E.; Kramer, E. J.; Osby, J. O. *Macromolecules* 1995, 28, 1979–1989.
- Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J Chem Phys* 1996, 105, 3777–3788.
- Lodge, T. P.; McLeish, T. C. B. *Macromolecules* 2000, 33, 5278–5284.
- Haley, J. C.; Lodge, T. P. *Colloid Polym Sci* 2004, 282, 793–801.
- Adams, S.; Adolf, D. B. *Macromolecules* 1999, 32, 3136–3145.
- Chung, G. C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* 1994, 27, 5729–5741.
- Chung, G. C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* 1994, 27, 964–973.
- Genix, A. C.; Arbe, A.; Alvarez, F.; Colmenero, J.; Willner, L.; Richter, D.; *Phys Rev E* 2005, 72, 031808.
- Haley, J. C.; Lodge, T. P.; He, Y. Y.; Ediger, M. D.; von Meerwall, E. D.; Mijovic, J. *Macromolecules* 2003, 36, 6142–6151.
- He, Y. Y.; Lutz, T. R.; Ediger, M. D. *Macromolecules* 2004, 37, 9889–9898.
- He, Y. Y.; Lutz, T. R.; Ediger, M. D. *J Chem Phys* 2003, 119, 9956–9965.
- He, Y. Y.; Lutz, T. R.; Ediger, M. D.; Lodge, T. P. *Macromolecules* 2003, 36, 9170–9175.
- He, Y. Y.; Lutz, T. R.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N.; von Meerwall, E. A. *Macromolecules* 2005, 38, 6216–6226.
- Lutz, T. R.; He, Y. Y.; Ediger, M. D.; Cao, H. H.; Lin, G. X.; Jones, A. A. *Macromolecules* 2003, 36, 1724–1730.
- Min, B. C.; Qiu, X. H.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* 2001, 34, 4466–4475.
- Miwa, Y.; Tanabe, T.; Yamamoto, K.; Sugino, Y.; Sakaguchi, M.; Sakai, M.; Shimada, S. *Macromolecules* 2004, 37, 8612–8617.
- Ngai, K. L.; Roland, C. M. *Macromolecules* 1995, 28, 4033–4035.
- Roland, C. M.; McGrath, K. J.; Casalini, R. *Macromolecules* 2006, 39, 3581–3587.
- Roovers, J.; Toporowski, P. M. *Macromolecules* 1992, 25, 1096–1102.
- Trask, C. A.; Roland, C. M. *Macromolecules* 1989, 22, 256–261.
- Sakaguchi, T.; Taniguchi, N.; Urakawa, O.; Adachi, K. *Macromolecules* 2005, 38, 422–428.
- Lodge, T. P.; Wood, E. R.; Haley, J. C. *J Polym Sci Part B: Polym Phys* 2006, 44, 756–763.
- Savin, D. A.; Larson, A. M.; Lodge, T. P. *J Polym Sci Part B: Polym Phys* 2004, 42, 1155–1163.
- Haley, J. C.; Lodge, T. R. *J Rheol* 2005, 49, 1277–1302.
- Lutz, T. R.; He, Y. Y.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* 2004, 37, 6440–6448.
- Nielsen, J. K.; Rasmussen, H. K.; Hassager, O.; McKinley, G. H. *J Rheol* 2006, 50, 453–476.
- Yang, X. P.; Halasa, A.; Hsu, W. L.; Wang, S. Q. *Macromolecules* 2001, 34, 8532–8540.
- Kim, J. K.; Lee, H. H.; Son, H. W.; Han, C. D. *Macromolecules* 1998, 31, 8566–8578.
- Tambasco, M.; Lipson, J. E. G.; Higgins, J. S. *Macromolecules* 2006, 39, 4860–4868.
- Bershtein, V. A.; Egorova, L. M.; Prudhomme, R. E. *J Macromol Sci Phys* 1997, 36, 513–533.
- Leroy, E.; Alegria, A.; Colmenero, J. *Macromolecules* 2003, 36, 7280–7288.
- Pathak, J. A.; Colby, R. H.; Floudas, G.; Jerome, R. *Macromolecules* 1999, 32, 2553–2561.
- Roland, C. M.; Ngai, K. L. *Macromolecules* 1992, 25, 363–367.
- Shimizu, H.; Horiuchi, S.; Kitano, T. *Macromolecules* 1999, 32, 537–540.
- Takegoshi, K.; Hikichi, K. *J Chem Phys* 1991, 94, 3200–3206.
- Wagler, T.; Rinaldi, P. L.; Han, C. D.; Chun, H. *Macromolecules* 2000, 33, 1778–1789.
- Cendoya, I.; Alegria, A.; Alberdi, J. M.; Colmenero, J.; Grimm, H.; Richter, D.; Frick, B. *Macromolecules* 1999, 32, 4065–4078.
- Green, P. F.; Adolf, D. B.; Gilliom, L. R. *Macromolecules* 1991, 24, 3377–3382.
- Kapnistos, M.; Hinrichs, A.; Vlassopoulos, D.; Anastasiadis, S. H.; Stammer, A.; Wolf, B. A. *Macromolecules* 1996, 29, 7155–7163.
- Kim, J. K.; Son, H. W. *Polymer* 1999, 40, 6789–6801.
- Kitade, S.; Ochiai, K.; Ida, M.; Takahashi, Y.; Noda, T. *Polym J* 1997, 29, 1034–1036.
- Kitade, S.; Takahashi, Y.; Noda, I. *Macromolecules* 1994, 27, 7397–7401.

43. Schacht, P. A.; Koberstein, J. T. *Polymer* 2002, 43, 6527–6534.
44. Radusch, H. J.; Tung, N. T.; Wohlfarth, C. *Angew Makromol Chem* 1996, 235, 175–191.
45. Lutz, T. R.; He, Y. Y.; Ediger, M. D. *Macromolecules* 2005, 38, 9826–9835.
46. Bovey, F. A.; Mirau, P. A. *NMR of Polymers*; American Press: San Diego, 1996.
47. Abragam, A. *The Principle of Nuclear Magnetism*; Clarendon Press: Oxford, 1961; Chapter III.
48. Heatley, F. *Prog Nucl Acid Magn Reson Spectrosc* 1979, 13, 47–85.
49. Loewenstein, A. In *Advances in Nuclear Quadrupole Resonance*; Smith, J. A. S., Ed.; Wiley: London, 1983; Vol. 5, pp 53–82.
50. Lucken, E. A. C. *Nuclear Quadrupole Coupling Constants*; Academic Press: London, 1969.
51. Williams, M. L.; Landel, R. F.; Ferry, L. J. *J Am Chem Soc* 1955, 77, 3701.
52. Tammann, G.; Hesse, W. *Z Anorg Allg Chem* 1926, 156, 245–257.
53. He, Y. Y.; Lutz, T. R.; Ediger, M. D.; Ayyagari, C.; Bedrov, D.; Smith, G. D. *Macromolecules* 2004, 37, 5032–5039.
54. Schneider, H. A.; Leikauf, B. *Thermochimica Acta* 1987, 114, 165–170.
55. Hirose, Y.; Urakawa, O.; Adachi, K. *Macromolecules* 2003, 36, 3699–3708.
56. Ediger, M. D.; Lutz, T. R.; He, Y. Y. *J Non-Crystal Solids* 2006, 352, 4718–4723.