Relaxation Dynamics in Poly(methylphenylsiloxane), 1,1-Bis(*p*-methoxyphenyl)cyclohexane, and Their Mixtures

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ABSTRACT: Mixtures of the small-molecule glass former 1,1-bis(*p*-methoxyphenyl)cyclohexane (BMC) with poly(methylphenylsiloxane) (PMPS) are especially interesting because the glass transition temperatures of the components are nearly equal.[1] Moreover, these T_g differences can be systematically varied by varying the molecular weight of the polymer. Dynamic mechanical measurements of the glass transition dispersion have been carried out on the neat liquids and their mixtures. The former exhibit normal segmental relaxation behavior, including a correlation of time and temperature dependences. While the behavior of the polymer-rich mixtures is unexceptional, the BMC dynamics are modified in a very interesting way by the presence of the polymer. In particular, the introduction of a small quantity of higher T_g PMPS is found to reduce the reorientational relaxation time of the BMC; that is, the relaxation speeds up. A similar anomaly has been observed in polychlorinated biphenyl containing a few percent of poly(vinylethylene).[2,3] This behavior is at odds with a simple free volume approach to relaxation in the vicinity of T_g; in fact, the excess volume is negative for BMC mixed with 10% PMPS. An interpretation for these results based on the coupling model of relaxation is suggested.

Introduction

In the free volume concept of segmental relaxation, the glass transition temperature governs the magnitude of the monomeric friction coefficient influencing the local dynamics.[4,5] In fact, T_g can be operationally defined as the temperature at which the segmental relaxation time assumes an arbitrary value (e.g., 100 s).[6,7] When measured at equal temperatures, segmental relaxation is slower for the polymer of higher glass transition temperature, congruent with larger local friction. The monomeric friction coefficient can be modified by the addition of a second component. Although the detailed consequences of mixing on the local dynamics are not completely understood,[8] the relaxation times measured for two liquids are expected to be closer in magnitude when blended than in their respective pure states. This underlies the expectation of single glass transitions in miscible blends. However, the homogeneous phase morphology of a miscible mixture does not necessarily give rise to equivalent relaxation times for the components. Such "dynamic heterogeneity" has been observed in polymer blends[9–11] and solutions.[12]

It is well-known that a polymer can be plasticized by the addition of solvent of lower T_g. In the rarer circumstance of the solvent having a higher glass transition temperature, the segmental relaxation time of the polymer is expected to increase (antiplasticization). The relaxation behavior of solvent-rich solutions obviously differs from that of the neat solvent. While traditionally the solvent is viewed as a Newtonian continuum making an additive contribution to the measured behavior, it has become clear that the solvent dynamics are directly modified by the presence of polymer.[8,13–15] Qualitatively, one anticipates a higher T_g polymer will increase the reorientational relaxation time of the solvent, while a lower T_g polymer will speed up the solvent relaxation. The most interesting situations arise when the glass transition temperatures of two components are nearly equivalent. Such mixtures provide a stern test for models of relaxation in the T_g region.

One recent example is the striking anomaly observed in polychlorinated biphenyl (PCB, trade-named Aroclor) containing a small quantity of poly(vinylethylene) (PVE). The reorientational relaxation time of the PCB is reduced by addition of the polymer, notwithstanding the latter's higher glass transition temperature.[2,3] An explanation for this phenomenon has been advanced based on the coupling model of relaxation,[16–18] in which the observed relaxation time, τ^*, is determined not only by the magnitude of the local friction coefficient but also by the degree to which the local motion is retarded by constraints from nonbonded neighboring molecules. Specifically, the coupling model predicts that the relaxation time will vary as

$$\tau^* = [(1-n)\omega_c^n\tau^0]^{1/(1-n)} \tag{1}$$

where the parameter n captures the strength of the intermolecular constraints on the relaxation and $1/\omega_c$ defines a characteristic time for the onset of the coupling (for polymers ω_c is typically of the order of 10^{11}–10^{12} s^{-1}). The relaxation time in the absence of intermolecular coupling, τ^0 (which for a long-chain molecule can be identified with the longer of the two relaxation times in the Hall–Helfand relaxation function[19,20]), has a magnitude governed primarily by the local friction factor.

Equation 1 reveals that when a strongly coupled (large n) polymer such as PVE is added to a weakly coupled, lower T_g liquid like PCB, the reorientational relaxation time of the latter may decrease. This is due to the fact that while strong intermolecular coupling is partially responsible for the high T_g of the PVE, this enhanced coupling of the neat polymer is irrelevant to the dynamics in a diluted state. Using eq 1, one can show that the friction coefficient, as reflected in the magnitude of τ^0, is less for

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PVE than for PCB; accordingly, addition of the former accelerates relaxation of the latter. Actually, recent results with higher molecular weight PVE reveal another source of the anomalous behavior in this mixture, originating from an excess mixing volume that is atypically positive.[3]

In general, the observed changes in relaxation times for mixtures may not parallel the respective glass transition temperatures of the pure components, particularly when the T_g's are close. This is due to the fact that the local friction coefficient is governed by the magnitude of τ^0 rather than τ^* (or the temperature at which τ^* assumes the value defining T_g). Of course, only the latter is actually measured in the neat components.

Mixtures of poly(methylphenylsiloxane) and BMC represent another interesting case, in that when the molecular weight of the polymer is about 20 000, the glass transition temperatures, as measured by DSC, are equal. Using probe molecules of the same size as the BMC, Lohfink and Sillescu[1] observed a dramatic change in the tracer diffusion constant upon addition of a small quantity of BMC to the PMPS. This indicates that the segmental dynamics of PMPS are strongly modified by the BMC, despite the equivalence of their glass transition temperatures. Stimulated by these results, we have carried out dynamic mechanical measurements in the vicinity of the glass transition temperature on BMC, PMPS of different molecular weights (and thus different T_g's), and both polymer- and BMC-rich mixtures.

Experimental Section

The BMC (or bisphenol-cyclohexane-dimethyl ether) was synthesized as described elsewhere.[21] It was filtered through 5-μm paper immediately prior to use; this slows down the crystallization rate presumably by removing nucleating impurities. The filtered BMC can be quenched without crystallization, as confirmed by DSC. Without this filtering, the relaxation behavior of BMC and the BMC-rich mixtures in the vicinity of T_g was poorly reproducible. The poly(methylphenylsiloxanes) were prepared by an anionic ring-opening polymerization of 1,3,5-trimethyl-1,3,5-diphenylcyclotrisiloxane. The full procedure and sample characterization are described elsewhere.[22] The number-average molecular weights, as determined by GPC, were 12 000 and 130 000 respectively for the polymers designated herein PMPS-l and PMPS-h. Polydispersities in both cases equaled 1.04.

Mixtures were obtained by dropwise addition of the BMC to thin films of the polymer. After absorption of the BMC, the mixture was annealed at least 24 h at 50 °C with periodic mechanical agitation, followed by room temperature annealing for 1 week.

Dynamic mechanical data in the vicinity of the glass transition zone were obtained with a Bohlin VOR rheometer using a parallel-plate geometry. Sample radii and gaps were typically 6 and 2 mm, respectively. The dynamic shear modulus was usually measured from 20 Hz down to as low as 1×10^{-4} Hz. The broad range of experimental frequencies obviated time-temperature superpositioning (which is usually not valid for blends[9-11,23-25] nor even for some neat polymers[26,27]). Prior to measurements at any given temperature, samples were maintained for a time period exceeding the anticipated relaxation time to minimize errors due to physical aging, an absence of which was affirmed by the reproducibility of measurements repeated after various time periods.

Results

A. Neat Liquids. Displayed in Figure 1 are representative measurements of the relaxation dispersion in the T_g region for the two siloxane polymers and for the BMC. The data were fitted to the well-known Kohlrausch-Williams-Watts stretched exponential function[28,29]

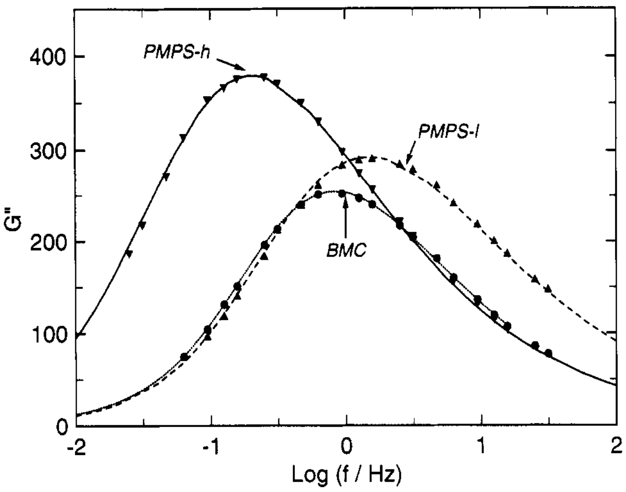

Figure 1. Dynamic mechanical loss moduli measured for the neat PMPS polymers and the BMC in the vicinity of their respective glass transition temperatures, along with the best-fit curve calculated using eqs 2 and 3. For the polymers, semilogarithmic plotting emphasizes the contribution of segmental motion and deemphasizes that of the Rouse modes.

$$E(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right] \qquad (2)$$

using

$$E''(\omega) = \omega \int_0^\infty E(t) \cos(\omega t)\, dt \qquad (3)$$

Although originally the KWW form was empirically derived, in the coupling model of relaxation the degree of nonexponentiality provides a measure of the strength of intermolecular coupling. Hence, for amorphous polymers, broader dispersions are associated with more intermolecular cooperativity, while a narrow dispersion implies weaker constraints from nonbonded neighbors on the relaxation. The obtained best-fit values for n were 0.44 for the neat BMC and 0.50 for either molecular weight PMPS. The magnitude of the coupling parameter was weakly dependent on temperature, varying no more than ±0.02 over the range of measurement temperatures. The n values obtained for BMC are consistent with, albeit slightly smaller than, those previously reported from dielectric spectroscopy measurements.[30] Although a dependence of the observed relaxation function on the experimental probe used to measure it would not be without precedent,[31-33] we believe at least part of the difference between the mechanical results herein and the earlier dielectric data[30] is due to the different manner in which the respective data, both obtained in the frequency domain, were fitted to the time-domain KWW function.[34]

The relaxation time of the neat liquids, defined as the inverse of the frequency of the maximum in G'', $(2\pi f_p)^{-1}$ (note that this quantity is very nearly equal to the τ^* obtained from the application of eq 2), is displayed in Figure 2. The lines through the data represent the best fit of the Vogel equation[5] (see Table I)

$$\tau^* = A \exp\left(\frac{B}{T - T_\infty}\right) \qquad (4)$$

Employing an operational definition of T_g as the temperature at which the relaxation time equals 100 s, we see in Table I that the glass transition temperature of BMC is intermediate between the T_g's of the two polymers. Although the latter have different glass transition temperatures (and hence different τ^* at any given temperature), as seen in Figure 1 the shape of the segmental

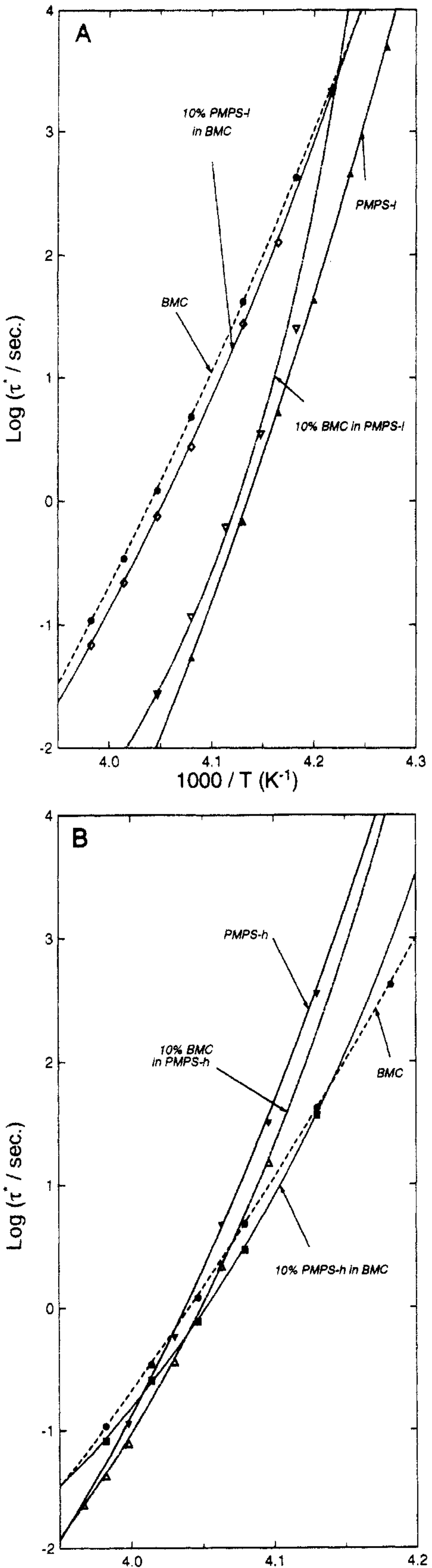

Figure 2. (A) Relaxation times (defined as $(2\pi f_p)^{-1}$, where f_p is the frequency of the maximum in the loss modulus dispersion) for BMC, PMPS-*l*, and their mixtures. Here and in (B), the solid curves represent the results of fitting eq 4 to the data, whose interpolation to $\tau^* = 100$ s yields a value for the glass transition temperature. (B) Relaxation times measured for BMC, PMPS-*h*, and their mixtures in the vicinity of the glass transition. BMC plasticizes the PMPS-*h* relaxation, while, over the range of the measurements, the higher T_g polymer reduces the relaxation time of the lower T_g BMC.

Table I. Results for Neat Liquids and Mixtures

	T_g,[a] K	log A	B	T_∞	n
BMC	241.0	−20.79	3556	173.2	0.44
PMPS-*l*	237.4	−21.96	2693	188.6	0.50
PMPS-*h*	243.2	−15.69	1414	208.5	0.50
90% BMC in PMPS-*l*	240.5	−15.16	1868	193.2	0.44
90% BMC in PMPS-*h*	240.9	−17.22	2427	186.0	0.44
10% BMC in PMPS-*l*	238.7	−7.43	303	224.7	0.51
10% BMC in PMPS-*h*	242.5	−10.47	667	219.3	0.48

[a] Corresponding to the temperature at which the mechanical relaxation time equals 100 s.

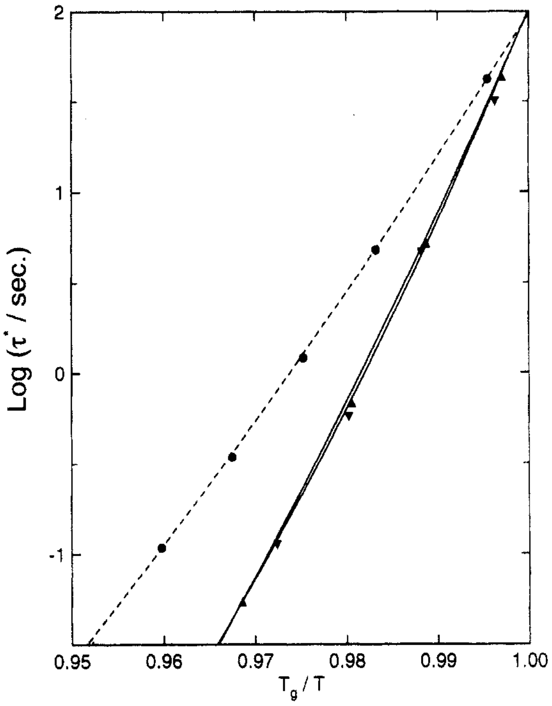

Figure 3. Relaxation times for the neat liquids displayed as a function of the inverse temperature normalized by T_g^{-1}. The steeper cooperativity plots for the polymers (solid curves) demonstrate that their segmental relaxation is more strongly coupled intermolecularly than the reorientational relaxation of BMC (dotted curve). The equivalence of the curves for PMPS-*l* and PMPS-*h*, consistent with the similarity of their coupling parameters, can be contrasted with their very different Arrhenius curves (Figure 2).

relaxation dispersion, and hence the degree of intermolecular coupling, is not a function of molecular weight. Rearranging eq 1 to give

$$\tau^* = (1-n)^{1/(1-n)}(\omega_c\tau^0)^{n/(1-n)}\tau^0 \qquad (5)$$

and recognizing that under the usual experimental conditions $\omega_c\tau^0 \gg 1$, it is seen that the temperature dependence of τ^* varies with the magnitude of the coupling parameter. Thus, the two siloxane polymers, with equal coupling parameters for their segmental relaxation, should have the same temperature dependence for τ^*. This is not directly evident in Figure 2, however, given the different measurement temperatures for the PMPS (appropriate to their respective T_g's). One cannot simply employ the slopes, or apparent activation energies, as a measure of the temperature dependence, because of the non-Arrhenius behavior.

T_g-scaled Arrhenius plots (log τ vs T_g/T) have been shown to be a rational means to classify the segmental relaxation characteristics of polymers.[35] This form was originally derived from the Adam and Gibbs model.[36–38] In Figure 3 the data from Figure 2 have been recast in the T_g-scaled form. This cooperativity plot[6,7,35,39] demon-

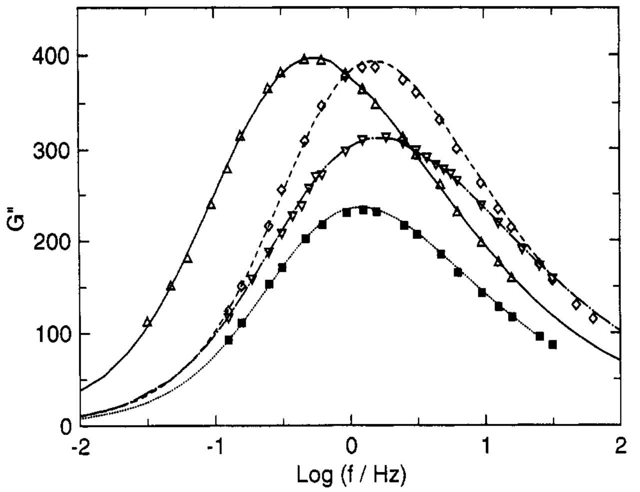

Figure 4. Dynamic mechanical loss moduli measured for BMC containing 10% of PMPS-*l* (open diamonds) and PMPS-*h* (filled squares), respectively, along with the corresponding results for the polymers containing 10% BMC (open triangles, right-side-up and inverted, respectively, for the mixtures with PMPS-*h* and PMPS-*l*).

strates that the segmental relaxation times of the two PMPS have the same normalized temperature dependences, an expected consequence of the equivalence of their coupling parameters (=0.50 ± 0.02 in Figure 1). While a difference in molecular weight produces different τ^0's and hence T_g's, the temperature dependence of τ^0 and the intermolecular coupling strength are both independent of molecular weight. This means that the dependence of the measured relaxation time on the normalized inverse temperature T_g/T will be independent of molecular weight, as seen in Figure 3.[35] Contrarily, the BMC, associated with weaker intermolecular constraints on its relaxation (n = 0.44), exhibits a weaker normalized temperature dependence in Figure 3.

B. BMC-Rich Mixtures. Displayed in Figure 4 are the dispersions measured for the mixtures in the vicinity of T_g. Although the distribution of local environments engendered by concentration fluctuations should broaden the loss modulus peaks relative to those of the neat liquids,[10,11,40–42] at 10% PMPS this effect is seen to make a minor contribution to the measured dispersion. This apparent absence of significant inhomogeneous broadening allows direct application of eq 2, even though in principle the viscoelastic spectra of blends will not exhibit the KWW shape.[10,11] The results (Figure 4) suggest that BMC containing 10% of either PMPS retains very nearly the coupling parameter observed for the neat BMC, n = 0.44. Of course, the possibility also exists that some inhomogeneous broadening is negated by a concurrent reduction in the intermolecular coupling of BMC upon addition of the polymer. BMC containing 10% of either PMPS may have a slightly smaller coupling parameter, with this reduction of n compensated by a modest inhomogeneous broadening.

In Figure 2 are the relaxation times measured at various temperatures for the mixtures, along with the best fit of eq 4 (Vogel parameters given in Table I). The addition of 10% PMPS-*l* to BMC reduces the latter's relaxation time, as expected simply from T_g considerations. Since the PMPS-*h* has a higher glass transition temperature than BMC, its addition might be expected to slow down BMC reorientation. On the contrary, however, at all temperatures the BMC relaxation time is observed to decrease upon addition of 10% PMPS-*h* (Figures 2b and 5).

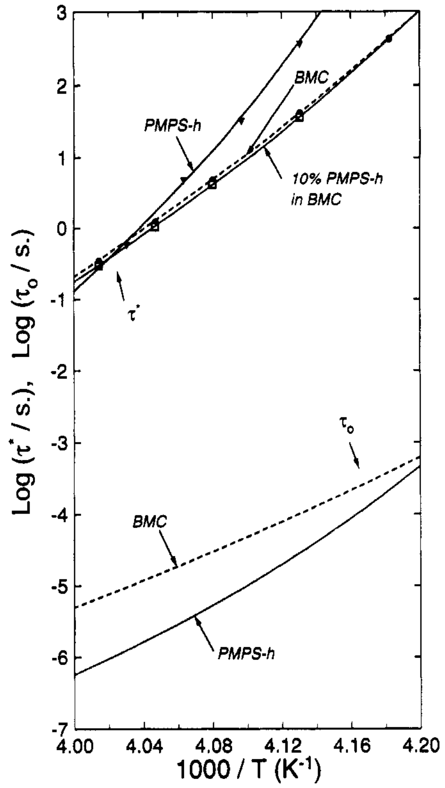

Figure 5. Relaxation times of neat BMC and PMPS-*h*, along with the results for a mixture containing 10% of the polymer. The lower curves represent the values of τ^0 calculated using eq 5 from the τ^* measured for the neat components. This reversal gives rise to the anomalous decrease in relaxation time of BMC upon addition of the higher T_g PMPS-*h*.

A similar anomaly appears in PCB/PVE mixtures, where again a higher T_g polymer increases the relaxation rate of a lower T_g small-molecule liquid. A hypothesis has been advanced to explain this unexpected modification of PCB's dynamics by addition of PVE.[2] This explanation assumes that a measure of the local friction in the mixture can be gained from the primitive relaxation time τ^0 (i.e., relaxation absent intermolecular coupling) deduced via eq 1 from measurements on the neat liquids. Because the neat polymer is associated with stronger intermolecular coupling than is the neat PCB, there is a reversal in the relative magnitudes of the relaxation times in going from τ^* to τ^0 via eq 1. Of course, such a calculation of τ^0 is only a "first-order" treatment, which circumvents detailed consideration of how the free volume and potential field arising from the local environment influence the actual τ^0 in the mixture.

Nevertheless, we apply eq 1 together with the n measured for the neat liquids to obtain at last qualitative predictions of the effect PMPS-*h* has on the BMC reorientational dynamics. Taking $10^{11} \leq \omega \leq 10^{12}$ Hz, τ^0 for BMC is found to be longer than the corresponding primitive relaxation time of PMPS-*h*, even though $\tau^*_{\mathrm{BMC}} < \tau^*_{\mathrm{PMPS}\text{-}h}$ (see Figure 5). Thus, 10% PMPS-*h* has the effect of decreasing the local friction, contributing to faster BMC relaxation. The anomalous decrease in BMC's relaxation time can be reconciled in terms of the reversal in the magnitude of the respective relaxation times upon removal of the effect of intermolecular coupling; i.e., $\tau^*_{\mathrm{BMC}} < \tau^*_{\mathrm{PMPS}\text{-}h}$ but $\tau^0_{\mathrm{BMC}} > \tau^0_{\mathrm{PMPS}}$ (Figure 5). The fact that $\tau^0_{\mathrm{BMC}} > \tau^0_{\mathrm{PMPS}}$ means that the guest polymer molecules have higher intrinsic (on the τ^0 level) mobility than that of the host BMC molecules, at least before cooperative constraint dynamics are considered. As a consequence, the guest polymer molecules will mitigate the mutual dynamic constraints

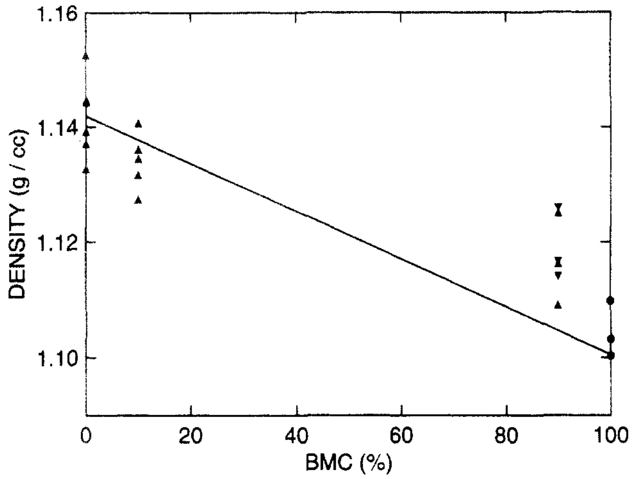

Figure 6. Density measured for the mixtures at room temperature (the symbols correspond to those in Figure 1). The solid line represents linear interpolation between the pure liquid densities. Note that addition of PMPS densifies the BMC, incongruent with the observed decrease of the latter's relaxation time. The polymer-rich mixture may be associated with a slight positive excess volume, but the result is not greater than the scatter in the data.

among the BMC molecules, leading to their faster motion (i.e., a decrease of $\tau^*_{\rm BMC}$ as described by eq 1 with a decrease in the coupling parameter).

In polymer solutions additivity of the volumes is not expected, and it must be recognized that a nonzero excess volume can contribute to changes in the relaxation times.[4,15] Although densification is more usual for mixtures of small molecules with polymers,[44,45] positive volume changes upon mixing are known.[46] In fact, such an effect has been shown to be operative in the PCB/PVE mixtures and is partially responsible for their anomalous relaxation behavior.[3]

In Figure 6 the density measured at room temperature is shown for neat BMC and PMPS-*h* as well as for the 10% mixtures. The excess volume, while very small, is negative for the BMC-rich solution. This would contribute to a slowing down of the BMC motion, notwithstanding the fact that experimentally the relaxation accelerates. Thus, the reversal in τ^0's discussed above (Figure 5) must be at least the primary, if not the only, factor governing the modification of BMC dynamics upon addition of the PMPS-*h*.

The cooperativity curves (not shown) corresponding to the data in Figure 2 are nearly the same for the BMC-rich mixtures as for neat BMC, consistent with the small change in the coupling parameter of BMC upon dilution (cf. Figures 1, 4, and 5). This is consistent with the notion that the intermolecular constraints on relaxation are not significantly modified upon addition of the polymer. In prior studies on polymer blends, it has been observed that a local environment associated with a higher (lower) T_g will increase (decrease) the intermolecular coupling.[11,25,43] This effect is minified herein due to the small differences in the component glass transition temperatures, along with their similar coupling parameters when neat. For this reason, when the temperature is lowered, the dispersion for the present mixtures does not exhibit the broadening toward low frequencies seen in more "dynamically heterogeneous" mixtures.[9,10,43]

C. PMPS-Rich Mixtures. The directional changes in the relaxation times of the polymers upon addition of 10% BMC show normal behavior; BMC plasticizes the higher T_g PMPS-*h* and antiplasticizes the lower T_g PMPS-*l*. This is "conventional" behavior insofar as it is consistent with the component glass transition temperatures; however, it begs the question why the reversal seen in the BMC-rich mixture ($\tau^*_{\rm BMC} < \tau^*_{\text{PMPS-}h}$ but $\tau^0_{\rm BMC} > \tau^0_{\text{PMPS-}h}$) is not observed for PMPS-*h* containing 10% BMC. The prediction from eq 1 of longer τ^0 for BMC than for PMPS-*h* suggests that upon addition of BMC there is an enhancement of intermolecular coupling for the segmental motions in PMPS with a concomitant increase in $\tau^*_{\text{PMPS-}h}$.

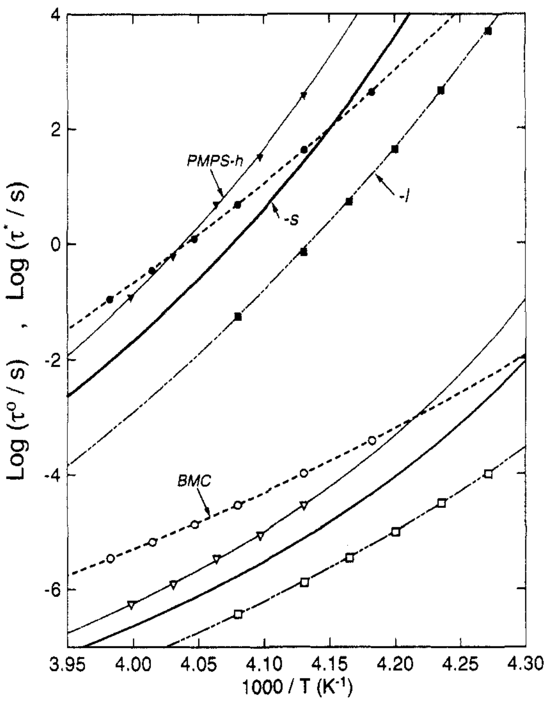

Figure 7. τ^*'s for three polymers with different molecular weights, PMPS-*h* (solid inverted triangles), PMPS-*s* (thick continuous curve), and PMPS-*l* (solid squares), and BMC (dashed line with solid circles). The corresponding τ^0's for these materials are indicated by the corresponding open symbols and the thinner continuous curve for PMPS-*s*.

It follows that 10% BMC should slow down segmental relaxation of PMPS-*h*; however, such anomalous antiplasticization of the PMPS-*h* is not observed. The data in Figure 6 hint that the polymer-rich mixture may be associated with a positive excess volume. Although the result is not significantly greater than the scatter in the measurements, it is tempting to infer that the absence of the predicted (eq 1) antiplasticization of PMPS-*h* upon addition of BMC is due to the additional free volume arising from mixing. In other words, the antiplasticization effect predicted from the coupling model is obscured by the plasticization effect caused by a positive excess volume.

This hypothesis can be tested by considering similar experimental measurements using PMPS samples with lower molecular weights and correspondingly lower T_g's. These samples will have shorter τ^0's than that of PMPS-*h* as illustrated in Figure 7 for PMPS-*l* and for a sample of PMPS (referred to as PMPS-*s*) that has the same T_g as that of BMC.[1] The τ^*'s and the calculated τ^0's of the three PMPS samples and BMC are shown in Figure 7. It is seen that the ratio $\tau^0_{\rm BMC}/\tau^0_{\rm PMPS}$ increases significantly when going from PMPS-*h* to PMPS-*s* to PMPS-*l*. We can conclude from the trend of this ratio that the predicted antiplasticization effect will be enhanced in PMPS-*s* and PMPS-*l* when compared to PMPS-*h*. This suggests that in PMPS-*s*-rich or PMPS-*l*-rich mixtures, the enhanced antiplasticization effect may overcome the plasticization coming from the positive excess volume.

Evidence of this stiuation can in fact be found in the tracer diffusion measurements of Lohfink and Sillescu on mixtures of PMPS-*s* and BMC.[1] They found that addition of BMC to PMPS substantially reduced the diffusion constant of a probe molecule having the same size as the BMC;[1] this is in direct contradiction to the consequences of an increase in volume upon mixing. The antiplasticization seen for 10% BMC in PMPS-*l* (Figure 2A), notwithstanding the positive excess volume of the mixture, provides additional support for an interpretation based on the second relation of the coupling model (eq 1). We also note in passing that the probe diffusion measurements of Lohfink and Sillescu in BMC-rich mixtures have also found an increase of mobility with addition of PMPS-*s* analogous to our mechanical relaxation data for BMC-rich mixtures of PMPS-*h*.

Similar to the results for BMC containing 10% polymer, the coupling parameters of both PMPS-*l* and PMPS-*h* are apparently little affected by mixing with BMC (see Table I). An invariant coupling parameter implies no change in T_g-normalized temperature dependence. In fact, there is a modest increase in the slope of the cooperativity plots (not shown) upon addition of 10% of the BMC. However, the temperature dependences of the PMPS and the BMC are very different (Figure 2), with the relaxation times of the PMPS-*l* and BMC converging at lower temperature. This suggests different temperature dependences of their respective conformation transition rates (i.e., $1/\tau^0$) resulting from their very different chemical structures. Promulgations of a correlation of time and temperature dependences[6,7,35,39] are strictly valid only for liquids with similar chemical structure, whereby the conformation transition rates in the absence of intermolecular coupling have similar temperature dependences. The cooperativity plot analysis neglects any contribution of differing τ^0 temperature dependences to the observed (i.e., τ^*) temperature dependences. Clearly, one cannot interpret differences in T_g-scaled temperature dependences between a hydrocarbon liquid and a siloxane polymer solely in terms of intermolecular constraints.

Summary

The data herein on the neat liquids corroborate previous results[6,7,35,39] demonstrating a correlation between the temperature dependence of the relaxation times and the magnitude of the coupling parameter describing the strength of the intermolecular constraints on the relaxation. In particular, for the siloxane polymers of different molecular weights and hence differing T_g's, normalizing temperature by the respective T_g's yields equivalent temperature dependences. This equivalence of their cooperativity plots is in accord with the equivalence in the shape of the segmental relaxation dispersions measured for the two polymers. The coupling parameter is smaller for BMC than for PMPS, and consequently its cooperativity plot is less steep. Although this is expected from eq 5, such a comparison between two liquids of different chemical backbone structure must be made with caution, given the possibility of a contribution from the temperature dependence of the primitive relaxation times (relaxation absent intermolecular correlations).[47]

For the BMC-rich mixtures we observe an anomaly—the addition of higher T_g PMPS-*h* reduces the BMC's relaxation time. This result is difficult to explain given that PMPS-*h* has a higher T_g than BMC and that the excess volume in BMC-rich PMPS solutions is negative (Figure 6). This anomaly can be rationalized from the second relation (eq 1) of the coupling model. The analysis shows that the monomeric friction coefficient, reflected in the value of τ^0, is smaller for PMPS-*h* than for BMC, notwithstanding the polymer's higher T_g. The value of T_g measured for a neat liquid is due in part to the contribution of intermolecular coupling to the observed relaxation time (i.e., τ^*). Intermolecular coupling is stronger in PMPS-*h* ($n = 0.50$) than in BMC ($n = 0.44$); thus, τ^* is longer even though $\tau^0_{\text{PMPS-}h} < \tau^0_{\text{BMC}}$. These results from mechanical spectroscopy are consistent with earlier probe diffusion experiments on mixtures of PMPS and BMC having equal glass transition temperatures.[1]

In PMPS-*h*-rich mixtures, we observe a positive excess volume which will speed up the PMPS-*h* segmental motion. The coupling model, based on a comparison of τ^0_{BMC} and $\tau^0_{\text{PMPS-}h}$, would predict slowing down of PMPS segmental relaxation upon addition of BMC. It is likely that in the PMPS-*h* mixtures, the change in volume upon mixing dominates, whereby segmental dynamics become faster than in pure PMPS-*h*. This situation is expected to be reversed in polymer-rich mixtures using lower molecular weight PMPS; the antiplasticization effect (eq 1) will overcome the plasticization coming from the positive excess volume. This expectation has been realized in an earlier study[1] on these materials, in which addition of BMC to PMPS drastically reduced (by more than a factor of 200) the diffusion constant of a probe molecule, with measurements carried out at $T = T_g$. Since the BMC and PMPS in this earlier study had the same glass transition temperature, the reduction was unexpected. The present data verify the probe diffusion result, in that we see using mechanical spectroscopy an acceleration of the solvent dynamics by addition of higher T_g polymer. Both the present and prior[1] results reflect the fact that the primitive relaxation time, τ^0, and the related monomeric friction coefficient are smaller for the polymer than BMC, notwithstanding the relative values of τ^* (or T_g) measured for the neat liquids. Hence, addition of BMC slows down probe diffusion, and addition of PMPS-*h* increases the relaxation rate of BMC. These results are consistent with the second relation of the coupling model (eq 1) and cannot *in toto* be otherwise explained.

An important point to bear in mind is that only through study of mixtures comprised of components of nearly equal T_g can the anomalies observed herein and elsewhere[1-3] be observed. In the more usual situation, a large difference in component glass transition temperatures overwhelms the more subtle effects arising from eq 1 or excess mixing volumes. In addition, the excess volume in mixtures needs to be further examined, for example by the use of direct experimental probes of free volume such as positronium annihilation lifetime spectroscopy and small-angle X-ray scattering.

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References and Notes

(1) Lohfink, M.; Sillescu, H. In *Proceedings of the 1st Tohwa University International Symposium*; Kawasaki, K., Kawakatsu, T., Tokuyama, M., Es.; American Institute of Physics: New York, 1992.

(2) Rizos, A.; Ngai, K. L. *Phys. Rev. B* **1992**, *46*, 8126.

(3) Santangelo, P. G.; Roland, C. M.; Ngai, K. L., to be published.

(4) Fujita, H. *Fortschr. Hochpolym.-Forsch.* **1961**, *3*, 1.

(5) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley, New York, 1980.

(6) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 5315.

(7) Plazek, D. J.; Ngai, K. L. *Macromolecules* **1991**, *24*, 1222.

(8) Lodge, T. P. *J. Phys. Chem.* **1993**, *97*, 1480.

(9) Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. *Macromolecules* **1990**, *23*, 4543.

(10) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.

(11) Roland, C. M.; Ngai, K. L. *J. Rheol.* **1992**, *36*, 1691.

(12) Plazek, D. J.; Seoul, C.; Bero, C. A. *J. Non-Cryst. Solids* **1991**, *131–133*, 570.

(13) Schrag, J. L.; et. al. *J. Non-Cryst. Solids* **1991**, *131–133*, 537.

(14) Gisser, D. J.; Ediger, M. D. *Macromolecules* **1992**, *25*, 1284.

(15) Fujita, H. *Macromolecules* **1993**, *26*, 643.

(16) Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. *Ann. N.Y. Acad. Sci.* **1986**, *484*, 150.

(17) Ngai, K. L.; Rendell, R. W. *J. Non-Cryst. Solids* **1991**, *131–133*, 942.

(18) Ngai, K. L.; Peng, S. L.; Tsang, K. Y. *Physica A* **1992**, *191*, 523.

(19) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.

(20) Ngai, K. L.; Rendell, R. W. *J. Non-Cryst. Solids* **1991**, *131–133*, 942–948.

(21) Gerharz, B.; Meier, G.; Fischer, E. W. *J. Chem. Phys.* **1990**, *92*, 7110.

(22) Momper, B.; Wagner, T.; Maschke, U.; Ballauff, M.; Fischer, E. W. *Polym. Commun.* **1990**, *31*, 286.

(23) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* **1988**, *21*, 2580.

(24) Colby, R. J. *Polymer* **1989**, *30*, 1275.

(25) Roland, C. M.; Ngai, K. L.; O'Reilly, J. M.; Sedita, J. S. *Macromolecules* **1992**, *25*, 3906.

(26) Plazek, D. J. *J. Phys. Chem.* **1965**, *69*, 3480.

(27) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 619.

(28) Kohlrausch, R. *Pogg. Ann. Phys.* **1847**, *12*, 393.

(29) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.

(30) Meier, G.; Gerharz, B.; Boese, D. *J. Non-Cryst. Solids* **1991**, *131–133*, 144.

(31) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymer Solids*; Wiley: London, 1967.

(32) Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988**, *21*, 3030.

(33) Santangelo, P. G.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1983**, *26*, 2682.

(34) The dielectric spectroscopy determinations of n in ref 30 were carried out by fitting the frequency dependence of the dielectric loss to the Havriliak–Negami form and then transforming this analytical representation of the data into the time domain. The latter were then fit directly to the KWW function (eq 2). This method weights the high- and low-frequency tails of the dispersion to a greater extent than direct fitting of the frequency data using eq 3. For the dielectric loss data of BMC, the transform of the Havriliak–Negami fit yields larger values of the coupling parameter ($n = 0.49 \pm 0.03$[30]) than the n we obtain by direct fitting of the same data in the frequency domain; the latter emphasizes more the peak of the dispersion and yields $n = 0.45$. This value is close to the coupling parameter determined herein from mechanical measurements on BMC.

(35) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 5765.

(36) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131–133*, 13.

(37) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.

(38) Ngai, K. L.; Rendell, R. W.; Plazek, J. *J. Chem. Phys.* **1991**, *94*, 3018.

(39) Roland, C. M. *Macromolecules* **1992**, *25*, 7031.

(40) Shears, M. S.; Williams, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 608.

(41) Wetton, R. E.; MacKnight, W. J.; Fried, J. R.; Karasz, F. E. *Macromolecules* **1978**, *11*, 158.

(42) Trask, C. A.; Roland, C. M. *Macromolecules* **1989**, *22*, 256.

(43) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363.

(44) Patterson, D. *Polym. Eng. Sci.* **1982**, *22*, 64.

(45) Maeda, Y.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1005.

(46) Flory, P. J. *Selected Works of Paul J. Flory*; Mandelkern, L., Mark, J. E., Suter, U. W., Yoon, D. Y., Eds.; Stanford Press: Stanford, CA, 1985; Vol. I.

(47) Ngai, K. L.; Roland, C. M. *Macromolecules*, submitted.