Segmental relaxation in miscible polymer blends

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Synopsis

Usually the shape of the glass transition dispersion in the mechanical or dielectric spectra of pure polymers is skewed toward higher frequencies. In miscible polymer blends not only is this peak broader than in pure polymers, the broadening is often asymmetric towards lower frequencies. Concentration fluctuations are the obvious source of the broadening; however, a simple distribution of relaxation times, corresponding to a distribution in local compositions, would not account for the reversal in the asymmetry of the dispersion. Miscible blends are also thermorheological complex, with the temperature dependence of segmental relaxation exhibiting idiosyncratic composition dependencies. A model to describe the composition dependence and shape of the relaxation spectra of miscible polymer blends in the glass transition zone is described. The fluctuations in local composition inherent to a miscible blend give rise to a distribution in both the relaxation time and degree of cooperativity of segmental relaxation. Generally, the intermolecular cooperativity will be amplified by a high relative abundance of the component of the blend with the higher glass transition temperature; at least for the blends studied herein, higher T_G is associated with a stronger capacity for intermolecular coupling of the segments. At fixed blend composition this effect governs the shape of the dispersion, as well as being manifested in the composition dependence of the segmental relaxation time. Since the response at lower frequency reflects the contribution of segments residing in regions richer in the high T_G component, it is anticipated that the glass transition dispersion in miscible blends will be asymmetrically broadened towards lower frequencies. Application of the model to some miscible blends, including poly(vinylethylene)/polyisoprene, polyvinylmethylether/polystyrene, and tetramethyl polycarbonate/polystyrene), is demonstrated to successfully describe their most prominent features.

INTRODUCTION

Relaxation of pure polymers near their glass transition usually has the Kohlrausch–Williams–Watts (KWW) form

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$$E(t)=(E_g-E_R)\exp\left[-\left(\frac{t}{\tau^*(n)}\right)^{1-n}\right]+E_R, \tag{1}$$

where E_g and E_R are the, respective, glassy and relaxed moduli, τ^* is an effective relaxation time, and n increases with the breadth of the relaxation dispersion. Ngai and Rendell (1991) and co-workers (1986) derived this relaxation function by introducing intermolecular cooperativity into expressions for the relaxation of isolated chains. The parameter n, referred to as the coupling parameter, is a measure of the strength of the intermolecular constraints. The fundamental relaxation mode of an isolated chain corresponds to intramolecularly correlated conformational transitions [Hall and Helfand (1982) and Bahar *et al.* (1991)]. In dense phase constraints from neighboring segments thwarts some of the attempted transitions. This cooperativity gives rise to random variations in the success rate for conformational transitions by the segments. At any given time on the molecular level the motions of individual segments are not identical nor do they proceed homogeneously. For a description of macroscopic variables we can consider an (average) transition rate which is retarded. The relaxation dynamics of experimentally observable quantities can be described in terms of a time-dependent relaxation rate, leading to the form of Eq. (1) [Ngai and co-workers (1986)].

RESULTS AND DISCUSSION

PVE/PIP blends

Before we discuss blends of poly(vinylethylene) PVE or 1,2-polybutadiene) and 1,4-polyisoprene (PIP), let us consider neat polybutadiene. The dynamic mechanical loss modulus measured in the glass transition zone for a series of polybutadienes of varying vinyl content (the 1,2-addition product) and for 1,4-polyisoprene was found by Roland and Ngai (1991) to be well described by Eq. (1). As seen in Fig. 1, the breadth of the dispersion was found to increase with increasing concentration of 1,2- chain units in the polymer backbone. The most heterogeneous chain structure, corresponding to random copolymers of 1,2- and 1,4- units, had a narrower dispersion than the pure 1,2-polybutadiene homopolymer. The breadth of the segmental relaxation dispersion in polybutadiene random copolymers depends strongly on composition because 1,4- and 1,2-butadiene have very different intrinsic propensities for intermolecular coupling. Polystyrene (PS) and poly-2-chlorostyrene (PoCS), on the other hand, have similar coupling param-

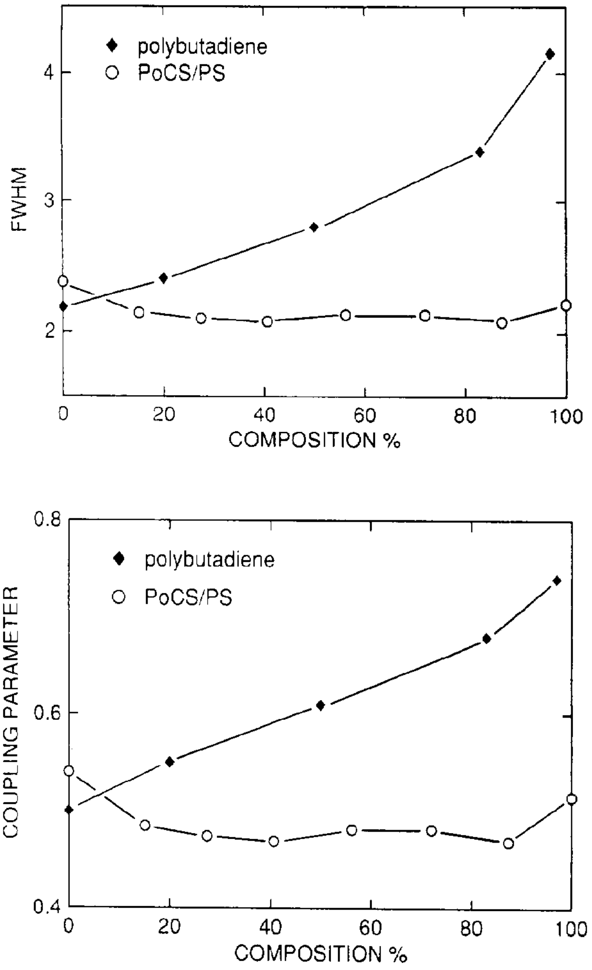

FIG. 1. The effect of copolymer composition on (a) the breadth (logarithm of the half width at half maximum in Hertz) of the segmental relaxation dispersion and (b) the best fit value for the coupling parameter [Eq. (1)] for random copolymers of butadiene [Roland and Ngai (1991)] and of styrene and 2-chlorostyrene [Alexandrovich *et al.* (1980)]. The abscissa refers to the concentration of the higher T_G component in the random copolymers. The large difference in coupling parameters between 1,4-butadiene and 1,2-butadiene causes n for their copolymers to depend strongly on copolymer composition. Contrarily, the similarity of polystyrene and poly-2-chlorostyrene in this regard causes segmental relaxation of their copolymers to exhibit comparable degrees of intermolecular coupling.

eters (indicated by the similarity of their dielectric loss curves) [Roland *et al.* (1982), Alexandrovich *et al.* (1980)]. Consequently, the segmental relaxation of their random copolymers should be similar to the PS and PoCS homopolymers, and be relatively independent of copolymer composition. As reported by Alexandrovich *et al.* (1980)], this is indeed the case (see Fig. 1).

The random copolymer results in Fig. 1 are in contradiction to any model that attempts to account for the shape of the segmental relaxation peak in terms of a distribution of relaxation times. Since chains having a significant concentration of both monomer units will be very structurally diverse, consideration of only intrachain conformational transition rates might lead to the expectation of a maximum in the dispersion breadth of polybutadiene as a function of vinyl content. The invariance to composition of the spectral breadths of random copolymers of styrene and 2-chlorostyrene is also difficult to reconcile with an inhomogeneous distribution of conformational transition rates as the primary origin of the shape of the glass transition dispersion in bulk polymers. In the coupling model approach, however, this invariance follows directly from the fact that styrene and 2-chlorostyrene chain units have comparable intermolecular coupling strengths (as seen from the similarity of the homopolymer segmental dispersions).

The coupling model of relaxation [Ngai and Rendell (1991)] relates the breadth of the segmental relaxation to the extent of intermolecular coupling between the local conformational transitions. The results for the polybutadienes [Roland and Ngai (1991)] then suggest that steric interactions among the inflexible vinyl moieties projecting from the main chain enhance the intermolecular coupling. As Plazek and Ngai (1991) have shown, the coupling model also predicts that there is a correlation between time and temperature dependencies of the relaxation. Specifically, polymer chains whose segmental relaxation is characterized by stronger intermolecular coupling (larger n) should exhibit a more marked dependence on temperature. This correlation of the frequency and temperature dependencies was observed by Roland and Ngai (1991) for the polydiene series.

The two polymers of the series exhibiting the most diverse relaxation behavior were 1,2-polybutadiene ($n=0.74$) and 1,4-polyisoprene ($n=0.50$). Since they form thermodynamically miscible blends devoid of specific interactions [Roland (1987), Roland (1988), Tomlin and Roland (1992)], PIP and PVE provide an interesting opportunity to investigate segmental relaxation in mixtures.

Unlike pure polymers, the segmental relaxation behavior of miscible blends does not usually conform to Eq. (1). In blends the glass transition dispersion is broader, often exhibiting an extraordinary low frequency tail, along with a strong temperature dependence. This broadening reflects the distribution of segment environments resulting from concentration fluctuations, the latter being inherent to miscible blends. The coupling model can be extended to include the effect of composition fluctuations on the relaxation behavior of blends in the glass transition zone. The distribution of local environments effects a distribution of coupling parameters; that is, concentration fluctuations affect the degree to which a given segment's relaxation involves neighboring chain units. The dependence of the relaxation rate on chemical structure, however, means that the segmental relaxation coupling parameters of the respective components are not necessarily equal in a blend. In order to calculate the dispersion expected for a blend, some assumption concerning the mechanical interaction of the local environments must be made. The extremes correspond to homogeneous stress and homogeneous strain, although the actual situation is more complex. If a uniformity of local strain condition is assumed, whereby the stress is additive, the mechanical loss spectra can be expressed as

$$E''(\omega)=\mathrm{Im}\sum_j \int_0^\infty \int_{n_l}^{n_u}\left(-\frac{d}{dt}\left\{\exp[a_j(\bar{n}_j-n)^2]\Delta E_j \times \exp\left[-\left(\frac{t}{\tau_j^*(\tau_j^0,n)}\right)^{1-n}\right]\right\}dn\right)\exp[-i\omega t]\,dt, \tag{2}$$

where ΔE_j, representing the contribution of the jth component to the measured response ($j=1$ or 2 for a binary blend), is proportional to concentration. In this equation $\bar{n}_j$ is the mean and a_j the variance of the coupling parameters, which are assumed to be normally distributed. This exact effect on n of a change in local composition is not known. The integration limits, n_l and n_u, connote the extremes in coupling strength of a component, which in principle range from $n=0$ (no intermolecular coupling) through $n=1$ (complete cessation of relaxation). In fact, the integration limits are determined by the extremes in local composition and the associated degrees of intermolecular coupling. On the right-hand side of Eq. (3), for each value of n in the normal distribution of the jth component the effective relaxation time $\tau^*(\tau_j^0,n)$ is calculated according to

$$\tau^*(\tau_j^0,n)=[(1-n)\omega_c^n\tau_j^0]^{1/(1-n)}, \tag{3}$$

where τ_j^0 is the relaxation time in the absence of intermolecular coupling. The Fourier transform of the time derivative of the correlation function $\exp[-(t/\tau^*(\tau_j^0,n))^{1-n}]$ is taken, then multiplied by the relaxation strength ΔE_j of the jth component. Taking the imaginary part gives the contribution to the loss modulus. Integrating this over the normal distribution of n (from the distribution in local environments) and summing over the j components yields the total response as a function of frequency.

For the sake of simplicity, a distribution of τ_j^0's, which may or may not be correlated with the distribution of n's, is not included in Eq. (3). For a detailed analysis of relaxation data from blends it may prove necessary to introduce such a distribution of τ_j^0's in future work. For present purposes only the effects that a distribution of coupling parameters would have on the blend dynamics is considered. This aspect is the focus herein because such a distribution of coupling parameters does not occur in pure (unblended) polymers. It is a novel feature of miscible blends. While a distribution of τ_j^0's is likely also present in blends given the distribution of local environments, an analysis of the combined effect of distributions in τ_j^0 and n is not readily carried out with the available data. Each τ_j^0 will have its own set of Vogel–Fulcher parameters to describe its temperature dependence. The profusion of factors necessary to be taken into account makes a unique theoretical description problematical at the present time. The coupling model approach to blend dynamics is necessary, however, in light of its singular ability to explain many properties observed in neat polymer dynamics. These properties remain unexplained by other approaches, such as those based on free volume.

Recently Fischer and Zetsche (1992) have constructed a model of blend dynamics based on a distribution of free volume approach. This model can reproduce the essential features of blend segmental dynamics (to be described below) as obtained through Eqs. (2) and (3) of our model. Additional experimental investigations of segmental dynamics in blends, particular wherein the components have different characteristics (e.g., different combinations of n and/or T_G), or a combined study of segmental and chain dynamics in the same blend [see, for example, Fytas *et al.* (1992)] are necessary to enable discrimination between different models.

The loss modulus peak associated with segmental relaxation is displayed in Fig. 2 for several PIP/PVE compositions. At high concentrations of PVE the breadth of the dispersion is very broad, extending over many decades of frequency [Trask and Roland (1989), Roland and

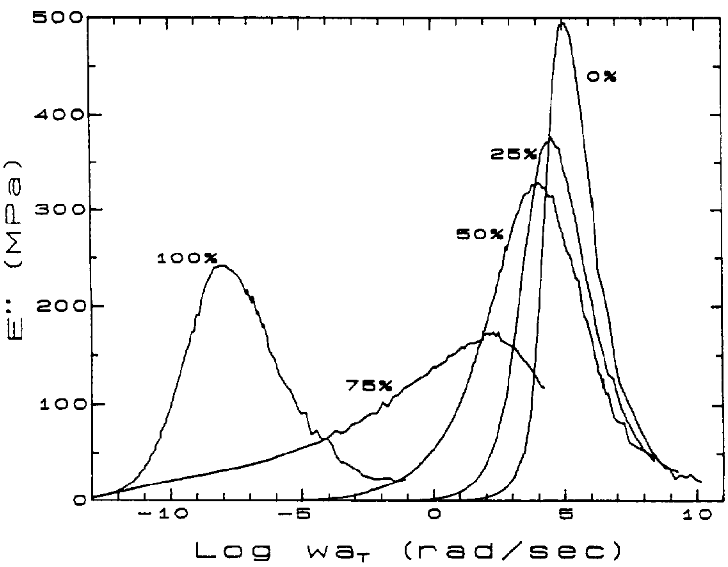

FIG. 2. The loss modulus spectra at a reference temperature of −40 °C for blends of PIP with the indicated concentration of PVE. The 75% PVE composition was extraordinarily broad, whereby the peak was not completely defined despite data having been obtained over a 95 deg range of temperatures.

Ngai (1991)]. By fitting Eq. (2) to the experimental data, a value for the average coupling parameter $\bar{n}$ for each component could be obtained as a function of blend composition. These results are shown in Fig. 3, which illustrates the fact that the degree of intermolecular cooperativity associated with a segment depends on the nature of both the segment as well as its surroundings. Consistent with NMR experiments on this mixture reported by Miller and co-workers (1990), the relaxation dynamics of PIP and PVE are not equivalent in the blend, the homogeneity of the average free volume and the gross morphology notwithstanding.

The salient features of the experimental data can be explained rather well with the approach embodied by Eq. (2). A PVE-rich environment is more effective in coupling to the primitive relaxation because of the higher coupling value for PVE segments (from Table I and Fig. 1 or 3, $n=0.74$ and $n=0.50$ for pure PVE and PIP, respectively). Additionally, since the glass transition temperature of PVE is 75 deg higher than

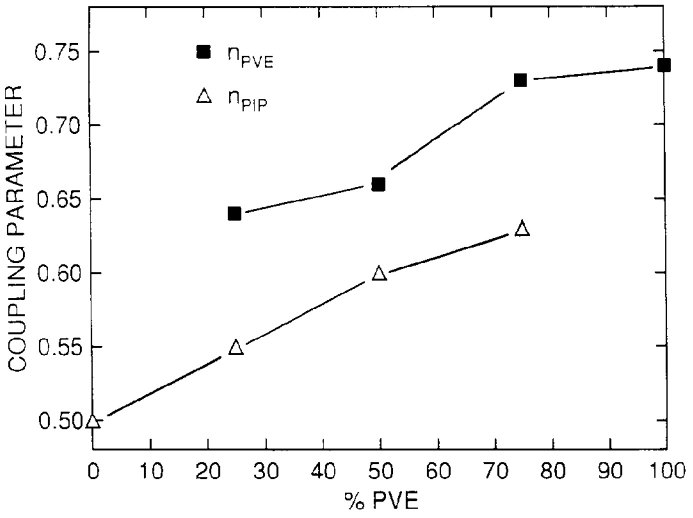

FIG. 3. The mean coupling parameter $\bar{n}$ determined for PIP and PVE, respectively, as a function of the composition of their blend.

that of PIP, PIP segments surrounded by PVE chain units will be relaxing in an environment that itself is relatively unrelaxed and thus unaccommodating. Hence, local environments richer in the PVE impose stronger intermolecular coupling and accordingly the broadening of the blend dispersion is accentuated on the low frequency side.

It is worth noting that if the effect of concentration fluctuations were only to displace the contributions from the segments to various posi-

TABLE I. Neat polymer properties.

	T_G (°C)	n
PVE	-1^a	0.74^a
PIP	-73^a	0.50^a
PVME	-16^b	0.56^b
TMPC	183^c	0.64^c
PS	90^c	0.46^c

[a] Mechanical spectroscopy [Roland and Ngai (1991)].
[b] Dielectric spectroscopy (using $\omega=1$ rad/s) [Roland and Ngai (1992)].
[c] Dielectric spectroscopy [Roland *et al.* (1992)].

tions about the peak frequency (i.e., inhomogeneous broadening without any concomitant distribution in the n_j), the spectral broadening would be symmetric. In fact, if each component relaxes according to Eq. (1), the spectral broadening would even be accentuated on the high frequency side, since a blend dispersion would be the superposition of numerous KWW functions. The asymmetry actually observed (skewing towards the low frequency side) is a direct consequence of a distribution in the intermolecular cooperativity resulting from the composition fluctuations.

PVME/PS blends

If one component of a blend is significantly more polar than the other, dielectric relaxation experiments can offer advantages over mechanical measurements for the study of blend dynamics. Poly(vinyl methyl ether) (PVME) has a much larger dipole moment than does polystyrene (PS), and thus it is the main contributor to the dielectric spectrum. From an analysis of dielectric measurements, the effect of local environment on segmental relaxation of PVME can be determined. The modification of Eq. (2) appropriate for dielectric data is in the absence of no local field effects:

$$\epsilon''(\omega)-\epsilon_{\infty}=\mathrm{Im}\sum_j\int_0^{\infty}\Delta\epsilon_j\int_{n_l}^{n_u}\left(-\frac{d}{dt}\left\{\exp[-a_j(\bar{n}_j-n)^2]\right.\right.$$
$$\left.\left.\times\exp\left[-\left(\frac{t}{\tau_j^*(\tau_j^0,n)}\right)^{1-n}\right]\right\}dn\right)\exp[-i\omega t]\,dt, \qquad (4)$$

where ϵ_{∞} is the high frequency permittivity and $\Delta\epsilon_j$ the dielectric relaxation strength of the *j*th component. Since PS is relatively nonpolar, the summation in Eq. (4) actually only includes PVME; that is, the dielectric spectra can be interpreted solely in terms of the effect of concentration fluctuations on relaxation of the PVME. Since frequencies across the spectral bands correspond to various τ^* reflecting the local composition, a value of the coupling parameter can be associated with a given frequency by fitting Eq. (4) to isothermal data obtained on a mixture whose composition was fixed at 60% by volume of PVME [Zetsche *et al.* (1990), Roland and Ngai (1992)]. The high frequency side of the dispersion reflects the PVME-rich environs, and the lower frequency response arises from PVME in PS-rich regions. A particular local composition can be identified with the frequency at which the integral intensity of the dielectric loss peak had decreased by a given amount, with the high (low) frequency side of the spectra corresponding to regions in which PVME (PS) is more concentrated.

From the analysis Roland and Ngai (1992) found the coupling parameter associated with local environments rich in PVME to equal 0.52, which is close to that of pure PVME ($n=0.56$). An increasing local concentration of PS has the effect of increasing the degree of intermolecular coupling, with a value of n as large as 0.75 deduced for PVME in PS-rich environs. Since the low frequency side of the dispersion represents the contribution of more coupled PVME segments, the spectral broadening occasioned by blending is again greater toward lower frequencies.

Interchain coupling of the segmental relaxation is expected to influence not only the shape of the relaxation function, but also its temperature dependence [Plazek and Ngai (1991)]. The temperature dependence of the relaxation times determined from fitting the PVME/PS dielectric data to Eq. (4) is shown in Fig. 4 in the form of Arrhenius plots, the temperature has been normalized by T_G. The latter is defined for the blend as the temperature at which $\epsilon''(\omega)$ has a maximum at $\omega=10^{-2}$ rad/s; this yields $T_G=256$ K for the blend. The $\epsilon''(\omega)$ maximum represents the response of segments whose local composition corresponds to the nominal blend composition. The temperature dependence of the data in Fig. 4 for various local compositions are normalized using this T_G. The validity of T_G-scaled Arrhenius plots of segmental relaxation times for glass forming liquids has been demonstrated from comparisons of data on polymers differing only in molecular weight [Roland and Ngai (1992)]. It is seen in Fig. 4 that the rank ordering of such cooperativity plots, each representing a different local composition, parallels the magnitude of the corresponding local coupling parameters. This agrees with previous results of Roland and Ngai (1991) and Plazek and Ngai (1991) on pure polymers, and is consistent with another prediction of the coupling model that more intermolecularly coupled relaxations will exhibit more marked temperature dependencies.

A glass transition temperature for neat PVME can similarly be defined as the temperature at which the central frequency corresponds to a relaxation time of 100 s; this yields $T_G=248$ K. The temperature dependence of the time–temperature shift factors of pure PVME has been included in Fig. 4. It is seen that the results for the blend, extracted by modeling the inhomogeneously broadened spectra, are consistent with the pure PVME result. The local blend composition whose shift factors have a temperature dependence similar to that of pure PVME is characterized by a similar coupling parameter. Note also in Fig. 4 that

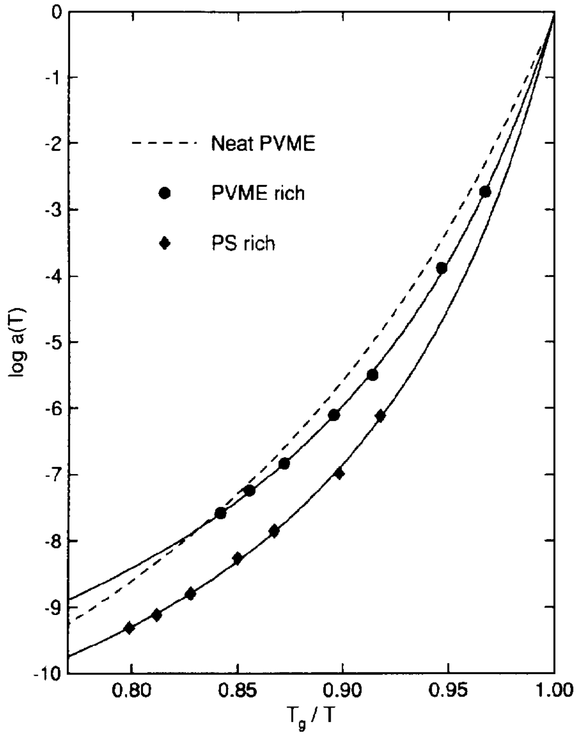

FIG. 4. The time–temperature shift factors, normalized by the value at the blend glass transition temperature (T_G=265 K), as a function of the inverse temperature normalized by T_G^{-1} for pure PVME (- -) and for the blend with 40% PS(—). The PVME-rich (PS-rich) curve refers to the shift factors for the high (low) frequency side of the glass transition dispersion, corresponding to a local composition richer in PVME (PS) than the average composition. The n associated with the PVME-rich region equals 0.52, which is close to that measured for pure PVME (n=0.56). For the PS-rich environment n=0.75.

the curves for both PVME blend compositions are steeper than that of pure PVME. This is due to the fact that PVME is being mixed with a polymer, PS, of much higher T_G. Blending increases the strength of the coupling and thus the temperature dependence of the relaxation.

TMPC/PS

Next we consider tetramethyl polycarbonate/polystyrene (TMPC/PS) blends. In the PVME/PS study described above only one blend (containing 60% PVME) was employed. Compositional variations corresponded to concentration fluctuation induced local environments within the blend. The variable n, characterizing the degree of intermolecular cooperativity associated with a given local environment, is different from $\bar{n}$ (the quantity displayed in Fig. 3 for the PIP/PVE blends). The latter represents the average coupling parameter for the mixture; that is, $\bar{n}$ is associated with a local composition equal to the bulk composition. From the discussion above $\bar{n}$ for PVME is expected to be a monotonically increasing function of the total PS concentration. Pure TMPC and pure PS have significantly different T_G's and coupling parameters [Roland *et al.* (1992)]. Segmental relaxation of TMPC in PS/TMPC blends should exhibit similarities to that of PVE in PIP/PVE blends and that of PS in PVME/PS blends. In the latter case, the coupling parameters measured dielectrically for pure PS and pure PVME are about the same; nevertheless, the large difference in component T_G is sufficient to cause differences in the strength of the intermolecular coupling of these components when blended. For TMPC/PS we expect that addition of PS molecules will reduce the coupling parameter for TMPC in any of its local environments in which PS replaces TMPC. This expectation is based on the fact that PS has less intrinsic propensity for intermolecular coupling (smaller dielectric n for the neat polymer) and a lower T_G than neat TMPC.

Dielectric spectroscopy is advantageous for this blend, since the response is dominated by the more polar TMPC. From an analysis of dielectric data obtained on TMPC/PS mixtures of various (average) composition, the temperature dependence of the segmental relaxation time can be determined for various $\bar{n}$. The available data for TMPC/PS blends are limited due to a narrower frequency window. The detailed analysis carried out for the PVME/PS data is neglected, and only the peak of the dielectric loss (representing a certain average local environment) is monitored. Hence, only the behavior of those TMPC segments which by virtue of their local environment govern the response at the dielectric loss maximum are considered. Blends with higher TMPC concentrations will have peak local environments higher in TMPC. It is anticipated that TMPC segmental relaxation of these peak local environments will be associated with larger coupling parameters. The time–temperature shift factors defined as

$$a_{\mathrm{TMPC}}(n,T)=\tau^{*}_{\mathrm{TMPC}}(n,T)/\tau^{*}_{\mathrm{TMPC}}(n,T_R) \tag{5}$$

(where T_R is an arbitrary reference temperature) depend on n as [Plazek and Ngai (1991)]

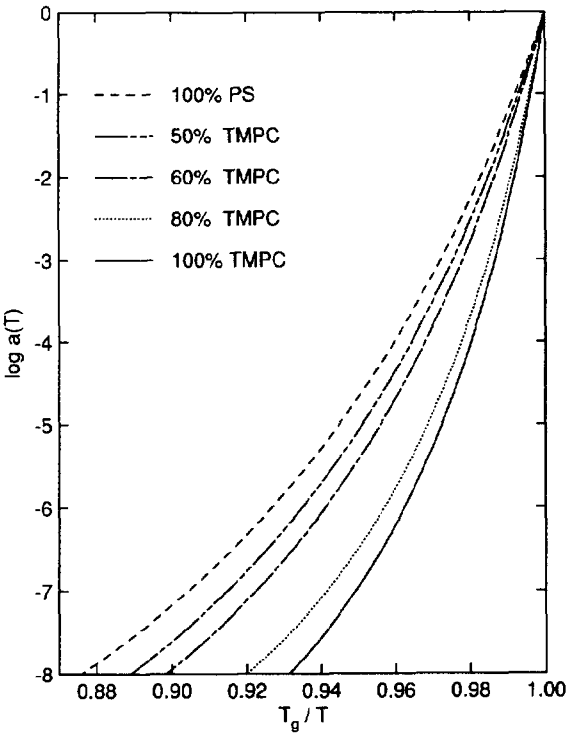

FIG. 5. The temperature dependence of the shift factors for the frequency associated with the peak local environments for the TMPC/PS mixtures with the indicated bulk composition.

$$\log[a_{\mathrm{TMPC}}(n,T)] = \left(\frac{1}{1-n}\right)\log a_{0,\mathrm{TMPC}}$$
$$= \left(\frac{1}{1-n}\right)\log[\tau_{0,\mathrm{TMPC}}(T)/\tau_{0,\mathrm{TMPC}}(T_0)], \qquad (6)$$

where $a_{0,\mathrm{TMPC}}$ represents the shift factors for the uncoupled (primitive) relaxation time $\tau_{0,\mathrm{TMPC}}$.

When the shift factors given by Eq. (5) are plotted in the form used in Fig. 5, it is seen that the pure TMPC has the strongest temperature dependence. Moreover, the temperature dependence is reduced in proportion to the concentration of PS in the blend. This corroborates the idea that more intermolecularly cooperative relaxations exhibit stronger temperature dependencies [Roland and Ngai (1991), Plazek and Ngai (1991)]. Unlike the approach used for the PVME/PS data, however, in Fig. 5 variations in cooperativity are achieved by changing the total blend composition.

PoCS/PS blends

In the three mixtures discussed above, the components have different T_G's and coupling parameters in the pure state. As discussed above, polystyrene and poly-2-chlorostyrene (PoCS) have comparable coupling parameters {indicated by the similarity of their dielectric loss curves [Roland, *et al.* (1992)]} and their T_G's differ by less than 30°. These features have direct consequences on the segmental relaxation behavior of their random copolymers (see Fig. 1), and should also be manifested in the properties of miscible blends of the two homopolymers. Alexandrovich and co-workers (1980) reported that the dielectric loss curve measured for a miscible blend of PS/PoCS is only slightly broader than the dielectric loss curve for the neat homopolymers. The reported temperature dependencies of the shift factors for the blend and the homopolymers are also nearly equivalent. These observations, that blending of polymers such as PS/PoCS does not significantly alter the components' intermolecular coupling, are consistent with the blend model presented herein.

SUMMARY

The shape of the $E''(\omega)$ and $\epsilon''(\omega)$ functions of miscible blends in glass transition zone, as well as both composition and temperature dependencies of the dispersion, are markedly influenced by the concentration fluctuations specific to miscible blends. Application of a model based for blends on the coupling scheme is demonstrated to successfully describe the prominent features of the measurements. The miscible blends, PVE/PIP, PS/PVME, and TMPC/PS, all exhibit similar segmental relaxation properties. Specifically, as the concentration of the latter components increase, a decrease of both the coupling parameter and the temperature dependence of the shift factor results.

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References

Alexandrovich, P. S., F. E. Karasz, and W. J. MacKnight, "Dielectric Study of Polymer Compatibility: Blends of Polystyrene/Poly-2-chlorostyrene," J. Macromol. Sci.-Phys. B **17**, 501–516 (1980).

Bahar, I., B. Erman, and L. Monnerie, "Stochastic Treatment of Conformational Transitions of Polymer Chains in the Sub-Rouse Regime," Macromolecules **24**, 3618–3626 (1991).

Fischer, E. and A. Zetsche, "Molecular Dynamics in Polymer Mixtures near the Glass Transition as Measured by Dielectric Relaxation," Polym. Prepr. **33**, 78–79 (1992).

Fytas, G., I. Alig., A. Rizos, J. Kanetakis, and F. Kremer, "Segmental and Chain Dynamics in Disordered Block Copolymers," Polym. Prepr. **33**, 86–87 (1992).

Hall, C. K. and Helfand, E., "Conformational State Relaxation in Polymers: Time-Correlation Functions," J. Chem. Phys. 77, 3275–3282 (1982).

Miller, J. B., K. J. McGrath, C. M. Roland, C. A. Trask, and A. N. Garroway, "Nuclear Magnetic Resonance Study of Polyisopme/Poly(vinylethlene) Miscible Blends," Macromolecules **23**, 4543–4547 (1990).

Ngai, K. L., R. W. Rendell, A. K. Rajagopal, and S. Teitler, "Three Coupled Relations for Relaxations in Complex Systems," Ann. N. Y. Acad. Sci. **484**, 150–184 (1986).

Ngai, K. L. and R. W. Rendell, "From Conformational Transitions in a Polymer Chain to Segmental Relaxation in a Bulk Polymer," J. Non-Cryst. Solids **131–133**, 942–948 (1991).

Plazek, D. J. and K. L. Ngai, "Correlation of Polymer Segmental Chain Dynamics with Temperature-Dependent Time-Scale Shifts," Macromolecules **24**, 1222–1224 (1991).

Roland, C. M., "Entropically Driven Miscibility in a Blend of High Molecular Weight Polymers," Macromolecules **20**, 2557–2563 (1987).

Roland, C. M., "Rheology of a Miscible Polymer Blend," J. Polym. Sci. Polym. Phys. Ed. **26**, 839–856 (1988).

Roland, C. M. and K. L. Ngai, "Segmental Relaxation and Molecular Structure in Polybutadienes and Polyisoprene," Macromolecules **24**, 5315–5319 (1991).

Roland, C. M. and K. L. Ngai, "Dynamic Heterogeneity in a Miscible Polymer Blend," Macromolecules **24**, 2261–2265 (1991).

Roland, C. M., K. L. Ngai, J. M. O'Reilly, and J. S. Sedita, "Trends in the Temperature Dependency of Segmental Relaxation in TMPC/PS Blends," Macromolecules **25**, 3906 (1992).

Roland, C. M. and K. L. Ngai, "Segmental Relaxation and the Correlation of Time and Temperature Dependencies in Poly(vinyl methyl ether)/Polystyrene Mixtures," Macromolecules **25**, 363–367 (1992).

Roland, C. M. and K. L. Ngai, "Normalization of the Temperature Dependence of Segmental Relaxation Times," Macromolecules (in press).

Tomlin, D. W. and C. M. Roland, "Negative Excess Enthalpy in a van der Waals Polymer Mixture," Macromolecules **25**, 2994–2996 (1992).

Trask, C. A. and C. M. Roland, "A Nearly Ideal Mixture of High Polymers," Macromolecules **22**, 256–261 (1989).

Zetsche, A., F. Kremer, W. Jung, and H. Schulze, "Dielectric Study on the Miscibility of Binary Polymer Blends," Polymer **31**, 1883–1887 (1990).