

Trends in the Temperature Dependency of Segmental Relaxation in TMPC/PS Blends

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ABSTRACT: A model to account for the composition dependence and shape of the relaxation spectra of miscible blends in the glass transition zone is applied to dielectric measurements on tetramethyl-Bisphenol A polycarbonate (TMPC) mixed with polystyrene (PS). The shape of the dispersion associated with segmental relaxation is governed primarily by the fluctuations in the degree of cooperativity associated with the distribution in local composition arising from concentration fluctuations. A blend of fixed composition possesses a distribution of local environments; these effect a distribution in the degree of cooperativity of the segmental relaxation of locally rearranging chain units. Pure PS has a lower T_g than TMPC. Hence, in the blend before cooperative dynamics is considered, PS chains will tend to have segmentally relaxed when segmental relaxation of TMPC is considered. The dynamical constraints imposed by PS segments in a local environment of TMPC are thus mitigated, allowing TMPC segmental relaxation to proceed with a lower degree of intermolecular cooperativity than is the case in less PS-rich environments. The temperature dependence of the frequency-temperature shift factors for the blend are governed by the degree of intermolecular cooperativity of the segmental relaxation. Hence, there exists a direct and verifiable relation between frequency and temperature dependencies of the mixture. The present data on TMPC/PS, though not sufficient to entirely demonstrate such a relationship, are nevertheless consistent with the predicted relation.

Introduction

Miscible polymer blends reveal new physics not encountered in neat polymers.¹⁻⁷ Their segmental relaxation behavior, for example, is an intriguing area of research. The mechanical and dielectric glass transition dispersions in some miscible blends are unusually broad, exhibiting an extraordinary low-frequency tail and a strong temperature dependence. These characteristics are seen in miscible blends of 1,4-polyisoprene and poly(vinyl-ethylene),¹⁻³ as well as poly(vinyl methyl ether) and polystyrene,⁴ which will be referred to as PIP/PVE and PVME/PS, respectively. Although this behavior is closely related to the distribution of segment environments arising from concentration fluctuations, the construction of a theoretical model to describe the segmental dynamics of the blend is a nontrivial task. The salient features of segmental relaxation in these blends have been explained rather well by an extension of the coupling model of relaxation.⁸ In blends of PIP/PVE, environments richer in the latter confer to locally rearranging segments a larger degree of intermolecular coupling (stronger intermolecular constraints), due to the higher T_g and intrinsically greater capacity for strong intermolecular coupling of pure PVE. In a pure polymer the strength of the intermolecular coupling of segmental relaxation depends on the chemical structure of the monomer units.⁹ In PVE the inflexible vinyl moieties projecting from the chain units induce larger intermolecular coupling than occurs in 1,4-polyisoprene (PIP), whose unsaturated carbons are part of the chain backbone. Dynamic mechanical measurements have directly demonstrated that the coupling parameter, which provides a measure of the strength of the intermolecular coupling, is larger in PVE ($n = 0.74$) than for PIP ($n = 0.50$).¹

From dielectric relaxation measurements it is known that neat PVME and PS have comparable coupling parameters.¹⁰ In their blends, therefore, it is principally the slower rate of intramolecular conformational transi-

tions by PS (due to its higher glass transition temperature) that causes PVME in environments richer in PS to have larger intermolecular coupling and, consequently, be associated with larger values of the coupling parameter.

Dielectric relaxation studies of blends offer advantages over mechanical measurements since in favorable cases one component will be the main contributor to the dielectric spectrum. Since PVME has a much larger dipole moment than does PS, PVME dominates the dielectric response of their blends. Dielectric spectra from these blends can provide information on the influence of local environment on the segmental relaxation of PVME. By utilizing the coupling model to analyze isothermal data taken at various temperatures, the dependence of n of PVME on local composition was deduced.⁴ The coupling parameter associated with local environments rich in PVME is found to be close to that of pure PVME (ca. 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 some PS-rich environments. The coupling model also offers the verifiable prediction of a correlation between the n 's and the temperature dependencies of segmental relaxation for PVME in the various local environments. The anticipated correlation was borne out by the experimental data. The PS segmental dynamics in the same blend could not be measured in this dielectric investigation. However, theoretically we can describe the frequency and temperature dependencies of segmental dynamics of PS in the various local environment and the trends of their variations with blend composition.

Recently, another miscible blend of TMPC and PS was studied using dielectric spectroscopy.^{11,12} At 1 kHz, the maximum loss tangent of pure TMPC is about a factor of 10 larger than that of pure PS, implying that TMPC dominates the dielectric response of the blends except at low TMPC concentration. With respect to coupling, TMPC plays the role of PS in PS/PVME blends. Hence,

the situation that we can theoretically describe segmental dynamics of PS which could not be measured is circumvented by study of TMPC segmental relaxation in the TMPC/PS blend. In fact the data obtained on the segmental relaxation of TMPC in TMPC/PS blends reveal a somewhat different manifestation of the effect of concentration fluctuations from the results seen previously for PVME in PVME/PS blends and PIP in PIP/PVE blends. In this paper, the properties of segmental relaxation of TMPC in TMPC/PS will be discussed with emphasis on differences from the behavior of PVME relaxation seen in PVME/PS blends. Predictions of the coupling model are compared with the dielectric relaxation data presently available.

Expected Properties of Segmental Relaxation of TMPC in TMPC/PS Blends

In the dielectric and enthalpy relaxation studies of TMPC/PS mixtures,^{11,12} measurements obtained on the pure components make evident that large differences exist between both the T_g 's and the coupling parameters of the two pure polymers. This is exactly the situation in the case of PVE/PIP¹ and PVME/PS.⁴ Segmental relaxation of TMPC in PS/TMPC blends should have properties similar to that of PVE in PIP/PVE blends and that of PS in PVME/PS blends. In the latter case, although the coupling parameters measured dielectrically for pure PS and pure PVME are about the same and only the condition of a large difference in T_g of the polymers holds, this condition is sufficient to effect significant differences in the intermolecular coupling strength of these components in the blend.

According to the coupling scheme, addition of PS molecules that have less intermolecular coupling (smaller n for pure PS) effectively lowers the coupling parameter for TMPC segmental relaxation in any of its local environments in which PS replaces TMPC. In addition, the fact that pure PS has a lower T_g implies that in the blend PS chains will tend to be segmentally relaxed when segmental relaxation of TMPC is considered. Under this circumstance, the dynamical constraints imposed by the PS segments in a local environment of TMPC have been completely mitigated. A dynamic entropy formulation of the coupling scheme¹³ will lead to the conclusion that the coupling parameter n for TMPC segmental relaxation in that local environment of the blend is smaller than that of pure TMPC.

Due to the concentration fluctuations inherent to mixtures, a single blend of fixed composition possesses a myriad of local environments. This distribution of local environments effects a distribution of coupling parameters. According to the coupling scheme, TMPC segments in a local environment characterized by a coupling parameter n will relax in accordance with the Kohlrausch-Williams-Watts stretched exponential function^{8,13}

$$\phi_0(t) = \exp[-(t/\tau^*_{\text{TMPC}}(n))^{1-n}] \quad (1)$$

The apparent relaxation time $\tau^*_{\text{TMPC}}(n)$ is related to the coupling parameter n and τ^0_{TMPC} (one of the two relaxation times in the Hall-Helfand relaxation function that describes the segmental relaxation of a TMPC chain) as

$$\tau^*_{\text{TMPC}}(n) = [(1-n)\omega_c \tau^0_{\text{TMPC}}]^{1/(1-n)} \quad (2)$$

where $1/\omega_c$ defines a characteristic time for the intermolecular couplings to begin to manifest themselves (for neat polymers ω_c is typically of the order of 10^{10} to 10^{11} s⁻¹).⁸ The relaxation of TMPC segments is modeled with the assumption that concentration fluctuations produce a

Gaussian-distributed range of values for the coupling parameters reflecting the cooperative dynamics of their various local environments. The measured response is the sum over the distribution of n for all local environments. In the present case a smaller n in the distribution corresponds to local environments richer in PS than the average for the TMPC/PS blend. The experimental dielectric relaxation loss spectra measured isothermally at various temperatures are described using the expression

$$\epsilon''(\omega) = \text{Im} \int_0^\infty \Delta\epsilon_{\text{TMPC}} \int_0^1 -\frac{d}{dt} \{\exp[-a(n-\bar{n})^2] \times \exp[-(t/\tau^*_{\text{TMPC}}(\tau^0_{\text{TMPC}}, n))^{1-n}]\} \exp[-i\omega t] dt dn \quad (3)$$

where $\Delta\epsilon_{\text{TMPC}}$ is the TMPC relaxation strength, \bar{n} is the mean and a is the variance of the normal distribution of coupling parameters, and $\tau^*_{\text{TMPC}}(\tau^0_{\text{TMPC}}, n)$ ($\equiv \tau^*_{\text{TMPC}}(n)$) is calculated via eq 2. In addition to the distribution in coupling parameters, a distribution of τ^0_{TMPC} 's among the local environments is possible. For the sake of simplicity of representation, this possibility is not incorporated explicitly in eq 3. Furthermore, for the purpose of this paper, it is immaterial whether or not such a distribution is included. In eq 3, the contribution from PS has been neglected because $\Delta\epsilon_{\text{PS}}$ is small. However, this approximation is expected to break down in mixtures with low TMPC content, as is seen later.

It is important to distinguish between the variable n , characterizing the degree of intermolecular cooperativity associated with a given local environment, and \bar{n} , which represents the average coupling parameter for the mixture. From the discussion above \bar{n} is expected to be a monotonically decreasing function of the total PS concentration. Note that this \bar{n} is not obtainable by direct fitting of eq 1 to the measured segmental relaxation, since miscible blending gives rise to heterogeneous broadening of the dispersion, as described by eq 3. Generally, the relaxation function for blends will not conform to the form of the stretched exponential function.

Isothermal dielectric measurements carried out over a wide frequency range will bring out properties of $\epsilon''_{\text{TMPC}}(\omega)$ in the blend that can be anticipated from eqs 2 and 3. For example, consider the shift factors defined by

$$a_{\text{TMPC}}(n, T) = \tau^*_{\text{TMPC}}(n, T) / \tau^*_{\text{TMPC}}(n, T_R) \quad (4)$$

where T_R is an arbitrary reference temperature used to describe the temperature dependence of the effective relaxation time of segmental motion of TMPC in local environments having coupling parameter n . According to eq 2, these shift factors are related to the shift factors $a_{0, \text{TMPC}}$ for the primitive relaxation time τ^0_{TMPC} by

$$\log [a_{\text{TMPC}}(n, T)] = (1/(1-n)) \log a_{0, \text{TMPC}} = (1/(1-n)) \log [\tau_{0, \text{TMPC}}(T) / \tau_{0, \text{TMPC}}(T_0)] \quad (5)$$

Hence, the observed temperature dependence will be governed by the intermolecular cooperativity. From eq 5 it follows that TMPC segments in local environments richer in TMPC, characterized by stronger coupling (larger n), should exhibit a more marked dependence on temperature. It is also expected that the lower frequency (longer time) dielectric response arises from contributions of TMPC segments in local environments richer in TMPC. This is a direct consequence of eq 2 which predicts longer $\tau^*_{\text{TMPC}}(n)$ for larger n because, under the usual experimental conditions, the product $\omega_c \tau^0_{\text{TMPC}}$ is a number much greater than unity.

Table I

PS/TMPC	$T_{g,DSC}$ (°C)	T_g (°C)	c_1	c_2
100/0	104	90.3	10.1	51
80/20	115	112.3	11.0	28
50/50	136	130.5	12.0	42
40/60	142	139.7	12.7	35
20/80	162	160.8	11.7	22
0/100	192	183.2	8.9	29

Dielectric Relaxation Data

Small-angle neutron scattering measurements have been carried out on blends of PS and TMPC, from which the interaction parameter χ as well as the correlation length of the concentration fluctuations were determined.¹⁴ All χ values are negative over the composition range from 10/90 to 90/10. The correlation length of the concentration fluctuations is approximately twice the segment length of the components, implying that the mixing of this blend is effectively at the segmental level. The influence of concentration fluctuations on the relaxation behavior in mixtures is affected by this correlation length. Presumably, for a sufficiently small correlation length the concentration fluctuations will be averaged out with regard to their effect on segmental relaxation. This implication can only be assessed when dielectric measurements of segmental relaxation on TMPC/PS blends of various thermodynamic stability (various correlations lengths) become available. Dielectric measurements have been reported at various compositions in the range 1–100 kHz.^{11,12} Dielectric loss peaks were obtained by frequency-temperature superposition using the WLF equation

$$\log f(T) = \log f(T_{g,DSC}) - \frac{c_1(T - T_{g,DSC})}{c_2 + (T - T_{g,DSC})} \quad (6)$$

where $T_{g,DSC}$ is the calorimetric glass transition temperature measured at 20 deg/min. The parameters c_1 and c_2 in eq 6 were determined by nonlinear regression analysis of the logarithmic frequency versus the temperature of maximum loss data. These results have been reported elsewhere.^{11,12}

In this paper we follow previous work^{9,15} on segmental relaxation of pure polymers to define T_g as the temperature at which the relaxation time equals 100 s ($\tau^*(T_g) = 10^2$ s). From the relation, $\tau = (2\pi f)^{-1}$, between relaxation time and frequency and using eq 6, the following expression is obtained for the shift factor $a(T)$ ($\equiv \tau^*(T)/\tau(T_g)$)

$$\log a(T) = \log \tau(T_g) - 2.0 - \frac{c_1 T_g (x + \sigma)}{c_2 + T_g (x + \sigma)} \quad (7)$$

where

$$x = (T - T_g)/T_g \quad (8)$$

is the temperature difference variable normalized to T_g and

$$\sigma = \frac{T_{g,DSC} - T_g}{T_g} \quad (9)$$

The quantities $T_{g,DSC}$, c_1 , and c_2 given previously¹¹ and T_g determined here are listed in Table I for several blends and the pure polymers.

Results

The dielectric data presently available are not extensive enough to make a detailed analysis based on eq 3 worthwhile. Previously, this approach was used to deduce the coupling parameter associated with several local

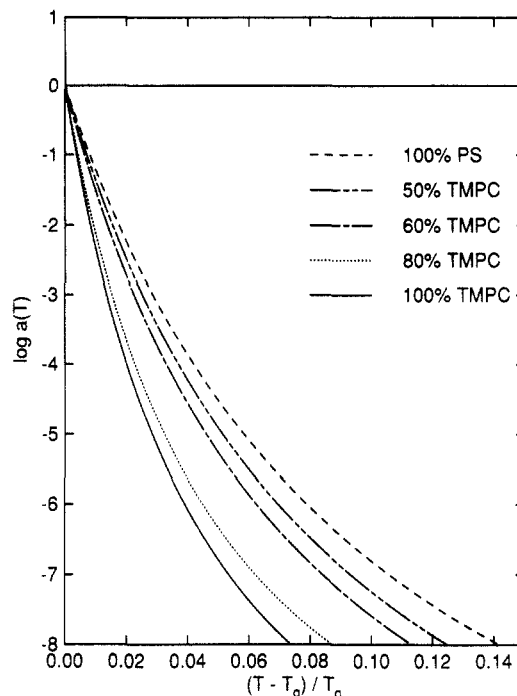


Figure 1. Temperature dependence of the shift factors for the frequency associated with the peak local environments for the indicated compositions.

environments (corresponding to different frequencies in the spectrum) for a single blend of PVME/PS.⁴ The variation of the coupling parameter across the dielectric dispersion conformed to expectations that the response at lower frequencies arises primarily from PVME segments in local environments having (1) a higher concentration of PS, (2) larger coupling parameters, and (3) a stronger temperature dependence of shift factor on the normalized inverse temperature T_g/T or the temperature difference variable $(T - T_g)/T_g$. We forgo such a detailed analysis herein; consideration will be limited to only those TMPC segments which by virtue of their local environment govern the response at the peak of the dielectric loss (henceforth referred to as "peak local environments"). From the data for various compositions of TMPC and PS a comparison can be made of the shift factors for the peak local environments and their temperature dependence.

Blends with higher TMPC concentrations will have peak local environments richer in TMPC; larger coupling parameters are expected for TMPC segmental relaxations of these peak local environments. From the dependence of the shift factor on n (eq 5), when the shift factors given by eq 7 are plotted versus $(T - T_g)/T_g$, the steepest variation is predicted for the composition with highest TMPC concentration; i.e., pure TMPC. Such plots are displayed in Figure 1, where it is seen that the rank ordering of the steepness of the curves representing different compositions indeed parallels their TMPC concentration. This agrees with previous results on pure polymers^{9,15} and blends⁴ and is consistent with the prediction of eq 5 that more intermolecularly coupled TMPC segmental relaxations will exhibit more marked temperature dependencies.

Omitted from Figure 1 is the data for the blend with 20% TMPC. The maximum loss tangent of this blend is only about 60% larger than the maximum loss tangent of pure PS. This indicates that it is no longer a good approximation to associate the dielectric loss only with TMPC segments; contributions from PS segments have to be included. It is expected that relaxation of PS

segments in this composition will have enhanced coupling parameters from that of pure PS and a concomitant steeper temperature variation with $(T - T_g)/T_g$. This expectation is in fact consistent with experiment when comparing the 20% TMPC blend with pure PS. Nevertheless, in order to avoid any confusion, data for the 20% TMPC blend has not been included in Figure 1.

Discussions and Summary

In miscible blends of TMPC and PS segmental relaxation of TMPC exhibits properties similar to those of segmental relaxations of PVE in PVE/PIP blends and PS in PS/PVME blends. These common features include (1) the decrease of the average coupling parameter (which may reflect the peak local environment) with decrease of TMPC content and (2) a concomitant decrease in the steepness of the shift factor with normalized temperature difference variable $(T - T_g)/T_g$, as illustrated for TMPC/PS blends in Figure 1. The dielectric studies of PVME/PS and TMPC/PS blends have in common the fact that segmental relaxations of PS are suppressed in the dielectric response of the blend; only segmental relaxation of the other component is monitored. However, the influence of blending on the spectral response is diametrically different for these two mixtures. For blends of PVME the lower frequency dielectric response is dominated by local environments richer in the *other* component (PS), whereas for TMPC this region of the spectrum reflects environments richer in the TMPC itself. The coupling parameter for PVME segmental relaxation in any local environment of the PVME/PS blend is always *larger* than that of pure PVME. Contrarily, the coupling of TMPC segmental relaxation in any local environment of the TMPC/PS blend is always *weaker* than that for pure TMPC. These differences between the two blends are brought out in the context of the coupling model, and the former are consistent with the latter.

The common characteristics of the segmental dynamics of the two blends are (1) the large increase in the breadth of the dielectric loss curves compared with those of the pure polymers, (2) an extraordinary low-frequency tail to the dispersion, particularly at lower temperatures, and (3) an expectation (not yet verified for TMPC/PS mixtures) of failure of time-temperature superpositioning. These properties, all consistent with predictions of the coupling model, result primarily from the large difference in the T_g 's of the pure components (~ 120 deg for PVME/PS and ~ 93 deg for TMPC/PS). For TMPC/PS, the larger intermolecular coupling intrinsic to TMPC molecules (dielectrically $n = 0.64$ for pure TMPC) compared with PS molecules (dielectrically $n = 0.46$ for pure PS) may also be a factor.

It is anticipated that a very different dielectric response would be measured from a miscible blend whose components have similar T_g 's and coupling parameters in the pure state. Miscible blends of polystyrene/poly-2-chlorostyrene (PS/PoCS) apparently are an example of this situation. The difference in T_g 's is less than 30 deg, and dielectrically, the two pure polymers evidently have about the same coupling parameters (as suggested by the fact that their dielectric loss curves have a similar shape and breadth). Indeed, dielectric data on blends of PS/PoCS reveal a different behavior.¹⁶ In miscible PS/PoCS blends only a slight increase in the width of the dielectric loss curves was observed compared to the neat polymers. Although the data are limited, the reported temperature dependencies of the shift factors for the blend and the neat polymers suggest that they are nearly equivalent when plotted against $(T - T_g)/T_g$ or T_g/T . This is in contrast to the large variation of the temperature dependency of the shift factor with blend composition observed in PVME/PS^{4,10} and TMPC/PS blends (Figure 1). It is tempting to call blends such as PS/PoCS "dynamically compatible", in the sense that intermolecular coupling of segmental relaxations of the pure polymers are relatively unaltered upon mixing.

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