

Broadband Dielectric Investigation on 2,6-Dihydroxynaphthalene/Poly(vinyl ethyl ether) Mixtures

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The relaxation dynamics of mixtures of 2,6-dihydroxynaphthalene and poly(vinyl ethyl ether) (DHN/PVEE), containing 1–20 wt % DHN, were investigated using dielectric relaxation spectroscopy (DRS). A single cooperative segmental relaxation was observed for all mixtures, which shifts to higher temperature and lower frequency upon addition of DHN. All mixtures are amorphous, as established by DSC. The fragility increases with DHN concentration, reflecting the combined contribution of the components. The modification of the DRS relaxation time of the PVEE α process by DHN was evaluated. Together with previously published data, a general feature of the influence of the guest component on the cooperative relaxation dynamics of the host in a miscible binary system becomes apparent: the influence of the guest approaches zero at approximately 60–100 °C above the T_g of the high T_g component, corresponding to the widely recognized critical temperature. The breadths of the α relaxations were found to be independent of temperature and composition. The small DHN molecules closely contact PVEE segments through intermolecular hydrogen bonding, and they are uniformly distributed in the PVEE matrix and have the same effect on all local environments of PVEE. The losses due to ionic conductivity exhibit the same shift factors for the α process in PVEE and all DHN/PVEE mixtures, suggesting that ion transport is highly coupled to the segmental relaxation of the polymer backbone.

Introduction

During the past several years, we have investigated the role of intermolecular hydrogen bonding on segmental and local dynamics of globally miscible polymer blends. Dielectric relaxation spectroscopy (DRS) was the principle tool used in these studies. Hydrogen bonding was found to damp concentration fluctuations, as revealed by the temperature-insensitive segmental relaxation time distribution in blends with appropriate compositions.¹ Intermolecular hydrogen bonding is also capable of coupling components' segmental relaxations in blends with large T_g differences, which would otherwise exhibit two segmental relaxation processes in the absence of strong intermolecular interactions. The coupling behavior is, however, composition-dependent and maximum coupling can only be achieved in blends dominated by inter-component associations. Dynamic heterogeneity still exists in blends controlled by intramolecular associations or with insufficient intermolecular hydrogen bonding. As expected, smaller dynamic asymmetry and stronger intermolecular interactions promote finer dynamic homogeneity.

To gain deeper insight regarding the role of intermolecular hydrogen bonding on component dynamics, as well as the nature of the glass transition, we have extended our studies to miscible polymer–solvent mixtures. There has been considerable research on the dynamics of polymer solutions having different concentrations,^{2,3} and small molecules have been used to probe relaxation dynamics of both other small molecules⁴ and polymers.⁵ Linkages between these glass-forming systems are being sought. In the present paper we investigate the influence of introducing a compound having low molar mass into a

polyether, with the former capable of forming two hydrogen bonds per molecule with the host polymer. We will show that excellent “matching” of the cooperative segmental relaxations of the two components can be achieved through suitable intercomponent interactions.

Experimental Section

Materials. Poly(vinyl ethyl ether) (PVEE) is a product of Monomer-Polymer & DAJAC Laboratories, Inc. This polymer has $M_w = 27\,000$ and M_w/M_n of 2.1, as determined by gel permeation chromatography using dimethylformamide/0.5% LiBr as the mobile phase and narrow molecular weight distribution poly(ethylene oxide)s as standards. 2,6-Dihydroxynaphthalene (DHN) was purchased from Aldrich and used without further purification.

PVEE was prepared by heating the polymer in vacuum at 50 °C for 1 day. Solutions consisting of 35 wt % DHN/PVEE in THF were cast onto Al foil. After most solvent had evaporated, the samples were heated in vacuum at 50 °C for a week. The Al foil was left on the samples. The mixtures are identified as Dx in the following text, where x is the wt % DHN in the mixture (based on the weight of PVEE). DHN content varies between 1 and 20% in this work.

Characterization. *Fourier Transform Infrared (FTIR) Spectroscopy.* Samples of the neat components and mixtures were cast onto KBr windows for FTIR analysis. FTIR spectra were obtained using a Bio-Rad FTS-6 spectrometer with a resolution of 2 cm^{-1} . Signals of 64 scans were averaged.

Differential Scanning Calorimetry (DSC). All DSC measurements were performed on a TA Instruments Q 100 apparatus. The temperature and transition enthalpy were calibrated with an indium standard. Samples of ~10 mg were scanned from –80 °C to 50 °C at 10 °C/min.

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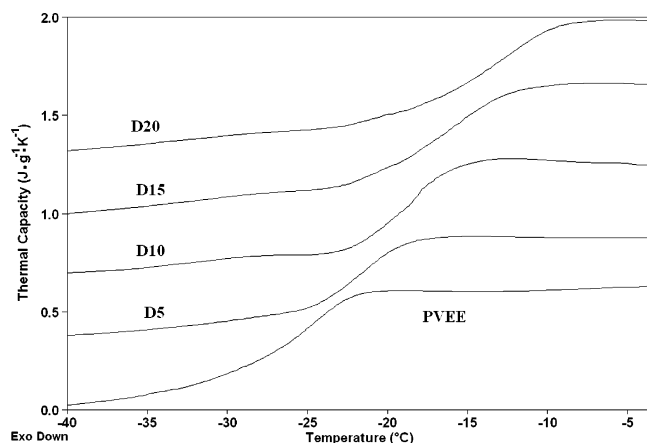


Figure 1. DSC thermograms of thermal capacity vs temperature for neat PVEE and DHN/PVEE mixtures. Heating rate is 10 °C/min.

TABLE 1: VFT Fitting Results of DRS Data, Compared with Those from DSC

	Pure PVEE	D5	D10	D15	D20
B (K)	2150	2160	2150	2120	2090
T_0 (°C)	181	186	191	199	205
fragility, m	66	67	68	71	74
$T(100\text{ s})$ (°C)	-34	-28	-24	-17	-11
DSC onset T_g (°C)	-30	-26	-22	-21	-19
DSC midpoint T_g (°C)	-25	-22	-18	-16	-13

Dielectric Relaxation Spectroscopy. DRS spectra were collected on a Novocontrol Concept 40 broadband dielectric spectrometer. Temperature was controlled through a Novocontrol Quatro Cryosystem. Experiments were run in the frequency domain [0.01 Hz–10 MHz], at 5 °C increments between -140 and 50 °C (± 0.3 °C stability). The minimum stabilization time at a given temperature was 1 min. Samples with a cross-sectional area a little larger than that of the upper electrode (20 mm) were sandwiched between two plate electrodes. Four small (~ 1.5 mm²) polypropylene spacers were used to control the sample thickness. The sample cell was purged with N₂ during the measurements.

Results and Discussion

Thermal Analysis. Neat DHN does not display a visible glass transition below its melting point (222 °C), even in a rapidly quenched sample. Nevertheless, DHN in mixtures with PVEE shows no signs of crystal melting and is consequently concluded to be in the amorphous state. Generally, for glass formers, the ratio of the melting temperature (T_m , K) to the glass transition temperature (T_g , K) has been estimated as about 1.3.⁶ This suggests a DHN T_g of ~ 108 °C, much higher than that of PVEE. A single T_g is observed in Figure 1 for all mixtures, which shifts gradually to higher temperature with increasing DHN content, in keeping with the DHN T_g estimated above. The transition interval does not change with DHN content, within experimental error. The midpoint and onset T_g values are reported in Table 1; the uncertainty in the T_g measurement is on the order of ± 2 °C.

FTIR. Figure 2 shows the region of the FTIR spectra of DHN and two representative mixtures of DHN with PVEE from 3620 to 3060 cm⁻¹. The -OH stretching absorption is located in the spectra of all mixtures at ~ 3310 cm⁻¹, much lower than that of that of unassociated ("free") -OH located at > 3520 cm⁻¹.^{1,7} The highly ordered structure of the DHN crystals leads to an intense -OH stretching vibration at an even lower frequency (~ 3260 cm⁻¹) (see Figure 2). The evidence strongly supports

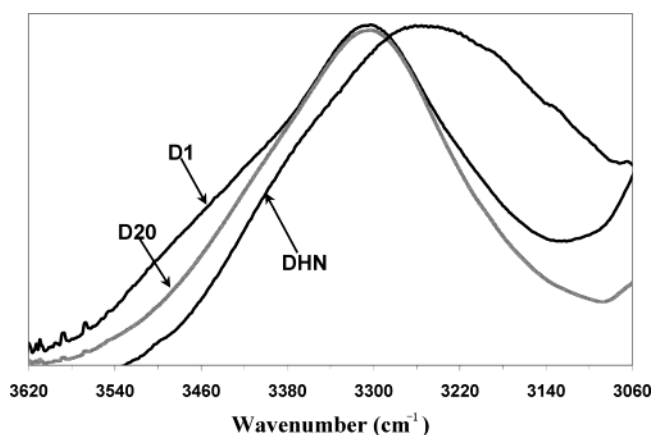


Figure 2. FTIR spectra at room temperature of DHN and two DHN/PVEE mixtures. The relative absorbance has been adjusted to approximately the same levels for presentation purposes.

that in all PVEE/DHN mixtures under investigation the preponderance of DHN molecules are hydrogen-bonded with PVEE.

DRS. The dielectric spectra of neat PVEE have been examined in some depth in earlier studies.⁸ PVEE exhibits a cooperative segmental (α) relaxation above T_g , which is broadened slightly toward higher frequencies, and follows the Vogel-Fulcher-Tammann (VFT) expression.⁹ A local β relaxation is also observed and is relatively weak. It has an Arrhenius temperature dependence with an activation energy of 20 kJ/mol, similar to that found for the β process of poly(vinyl methyl ether).¹⁰

PVEE and all DHN/PVEE mixtures in this work exhibit a single α process (Figure 3). Its strength appears to decrease with increasing temperature for neat PVEE. It is seen in Figure 4a that the α process gradually moves to lower frequency and higher temperature with increasing DHN content, and become more temperature sensitive after introduction of DHN. In contrast, the frequency-temperature (f - T) location of the sub- T_g β process is not affected by DHN within experimental error, as displayed in Figure 4b. However, with the addition of DHN, especially at $> 5\%$ DHN, the β loss peak broadens at low frequencies, and the fraction of the relatively slow process becomes larger the lower PVEE concentration. The results are similar to our previous observations for miscible poly(vinyl methyl ether) (PVME) mixtures with model low-molecular-weight compounds that hydrogen bond with PVME.¹¹ We propose that the existence of some slowly relaxing units is a result of the intermolecular hydrogen bonding of PVEE with DHN, as such interactions can increase the energy barrier for -OCH₂CH₃ rotation, the motion responsible for the PVEE β process. Suppression of a host polymer's local relaxation was also observed in our previous study of azo dye-PMMA solutions, which also involve intermolecular hydrogen bonding between the guest molecules and side groups of the host.¹²

The solid lines in Figure 4a represent best fits of the VFT expression:

$$f = f_0 e^{-B/(T-T_0)} \quad (1)$$

where f_0 , B , and T_0 are fitting parameters, and T_0 is the Vogel temperature. It can be seen that the VFT expression fits the experimental data well at all compositions.

The best-fit VFT parameters are summarized in Table 1. Angell previously proposed that the temperature at which the relaxation time for the fundamental enthalpic relaxation process

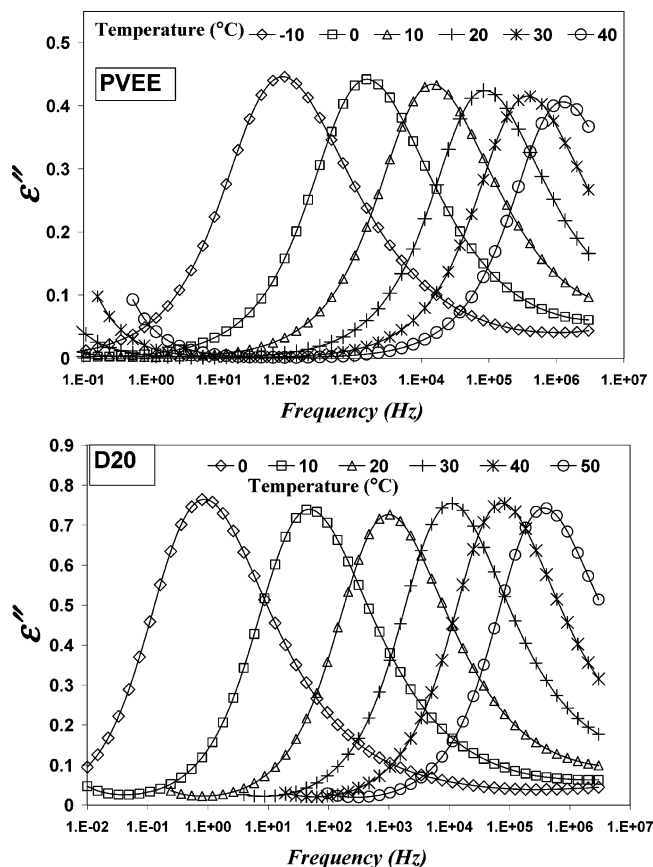


Figure 3. Dielectric loss ϵ'' vs frequency for the α process of (a) PVEE and (b) D20. The solid lines are only to guide the eyes.

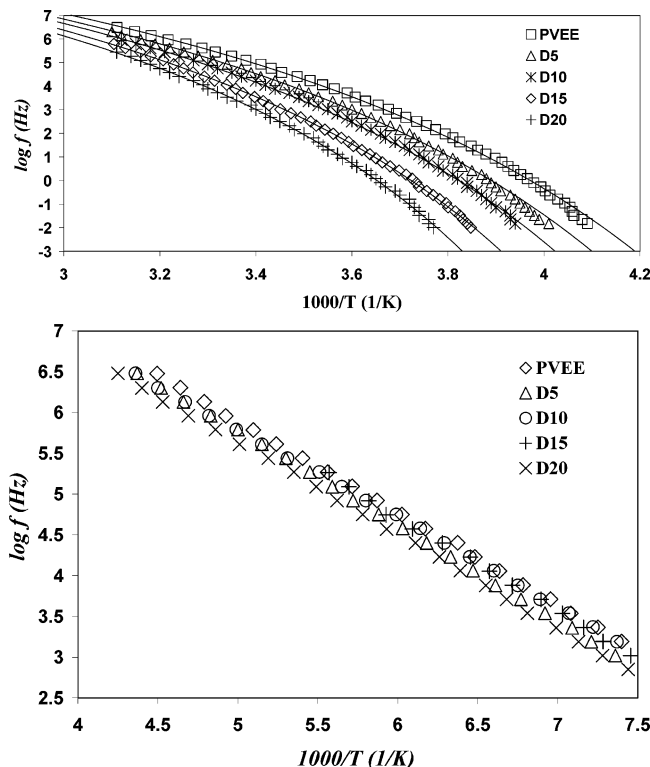


Figure 4. Arrhenius plots of $\log f$ vs $1/T$ of the dielectric relaxations in PVEE and DHN/PVEE mixtures: (a) α relaxation. The solid lines are VFT fitting results. (b) β relaxation.

reaches 100 s is close to the T_g obtained from standard scanning measurements, specifically the temperature at which the heat capacity jump characteristic of the glass transition commences

at a heating rate of 10 °C/min.¹³ The temperature at which the DRS relaxation time (τ) reaches 100 s ($T(100\text{ s})$) is comparable to the DSC onset T_g for neat PVEE, but the former becomes increasingly higher than the latter as DHN content increases. For D20, $T(100\text{ s})$ becomes comparable to the midpoint temperature of the heat capacity change through the T_g interval. Previously we found that there was a very good correlation between DRS $T(100\text{ s})$ and DSC onset T_g (10 °C/min) in amorphous poly(styrene-*co-p*-hydroxystyrene) (SHS)/ poly(ethylene oxide) (PEO) blends containing 60–100% SHS.¹ The chemical structures of SHS and PEO units are similar to those of DHN and PVEE, respectively, and intermolecular hydrogen bonds form in both systems. Consequently, it seems that the breakdown of this correlation in DHN/PVEE solutions is associated with the fact that DHN is a relatively small molecule, and therefore contributes differently to the onset T_g and the dipole moment change at $T(100\text{ s})$.

Fragility. The concept of fragility is used extensively to classify glass formers.¹⁴ It is a measure of the rapidity with which a material changes its mean relaxation time with temperature, and the extent of deviation of the relaxation times from simple Arrhenius behavior. The thermodynamic fragility, m , is popular and defined as

$$m = \frac{d \log \tau_{\max}}{d(T_{\text{ref}}/T)} \bigg|_{T=T_{\text{ref}}} \quad (2)$$

where T_{ref} is a reference temperature, which is normally close to T_g . Thus m describes the change in τ in the vicinity of T_g only. Replacing f with $1/(2\pi\tau)$ and taking the first derivative of the VFT expression and substituting leads to

$$m = \frac{B}{T_{\text{ref}} \times \ln 10 \times \left(1 - \frac{T_0}{T_{\text{ref}}}\right)^2} \quad (3)$$

The calculated m for PVEE and mixtures with DHN are reported in Table 1, and are seen to increase slightly with DHN content. According to the usual classification,¹⁵ relatively rigid DHN and flexible PVEE can be classified as fragile and strong glass formers, respectively. The gradually increasing fragility reflects the combined contribution of both components, which greatly affect the dynamics of one another due to the extensive miscibility, arising in part from intermolecular hydrogen bonding. The same behavior has been observed for a number of intermolecularly hydrogen-bonding polymer blends.¹ The similarity of the behavior of miscible polymer blends and polymer/small molecule solutions suggests that regardless of whether the participating units are polymer segments or small molecules, as long as the units are coupled their chemical structures are the primary factor determining the fragility of the multicomponent system.

DHN Influence on the Relaxation Time of PVEE. Lodge and colleagues have carried out detailed studies of the influence of dissolved polymer on solvent dynamics, primarily using depolarized Raleigh scattering and oscillatory electric birefringence experiments.^{2,16} They demonstrated that in a dilute polymer solution the influence (**I**) of the polymer solute (component **A**) on the dynamics of the small molecule solvent (component **B**) at a particular temperature, can be represented by the change in the relaxation time of component **B**, τ_B , with the concentration of component **A**, C_A , in the form

$$I_A = \frac{\partial}{\partial C_A} \ln \left[\frac{\tau_B(C_A, T)}{\tau_B(C_A = 0, T)} \right] \quad (4)$$

The fraction $\tau_B(C_A, T)/\tau_B(C_A = 0, T)$ was interpreted as the average effective friction coefficient ($= \zeta_B$) of component **B**.¹⁶ Equation 4 was obtained from the observation that the dependence of ζ_B on C_A follows an exponential form. Gisser and Ediger further proposed that

$$I_A = \frac{\partial}{\partial C_A} \ln \left[\frac{\tau_B(C_A, T)}{\tau_B(C_A = 0, T)} \right] = Q \log \left[\frac{\tau_A(C_A \rightarrow 0, T)}{\tau_B(C_A = 0, T)} \right] \quad (5)$$

¹⁷ where Q is an adjustable positive constant. In this case, **B** is a small solvent molecule, but component **A** is extended to small molecules as well as polymers. This approach was later extended to polyisoprene (PI)/poly(vinyl ethylene) (PVE) blends to scrutinize how the component polymers influence the relaxation dynamics of one another.¹⁸ The mutual influence of the components on the dynamics of PI/PVE blends was (re)analyzed along with additional experimental data in reference 19. The relation in eq 5 was followed in both studies. The implication is that eqs 4 and 5 have general meaning for various miscible mixtures of polymers and small molecules. Therefore, in the following discussion components **A** and **B** are simply designated as the guest and host, respectively.

In the present work we use I_A to characterize how DHN (guest **A**) influences the segmental relaxation of PVEE (host **B**). We assume that the volume of the mixture is that of the PVEE liquid phase, the density of which is 0.95 g/mL. Data for the α relaxations of PVEE, D5, and D10 were used in this analysis. Figure 5a displays the results of these calculations, and the temperature dependence is similar to that reported previously for the influence of other higher T_g components (HTC) on the lower T_g component (LTC).^{2,19} Above 50 °C, the frequency of the α relaxation exceeds the limit of our instrument. To further investigate the mechanism of how a miscible guest modifies the dynamics of a host, we analyzed experimental data in previous publications and noted an intriguing trend for all I_A data after normalizing the temperature by the T_g of the HTC.²⁰ As seen in Figure 5b, the influence of the guest (regardless of whether it is the high- or low- T_g component) on the host approaches zero at ~ 60 – 100 °C above the HTC T_g , corresponding to the widely recognized critical temperature (T_c).^{21,22} In a pure glass former, as temperature approaches T_c from above, the movement of each segment begins to be affected by spatially neighboring segments, which form a surrounding “cage”.²³ In binary mixtures, such cage effects may emerge when the temperature decreases below the T_c of the high T_g component, and modification of the dynamics of the host molecules becomes apparent, i.e., the alteration of the cage conditions by the other component speeds up or slows down the relaxations of the high and low T_g host components, respectively. In addition, as eq 5 suggests, when the temperature reaches T_c , $\tau_A(C_A \rightarrow 0, T)/\tau_B(C_A = 0, T) \sim 1$. It is interesting to note that, similar to the case of fragility, this conclusion is not affected by whether the components are small molecules or polymers.

It has been reported that the α process follows VFT behavior until it merges with the β process.^{6,24} For PVEE, the α/β merging temperature is ~ 110 °C, and it is even higher for DHN/PVEE mixtures since the f - T location of the β process is invariant with composition. Therefore we use the VFT relationship to estimate I_A for DHN/PVEE blends up to 110 °C. This is shown in Figure 5b by the solid line, and the results also reasonably follow the tendency for $I_A \rightarrow 0$ as temperature

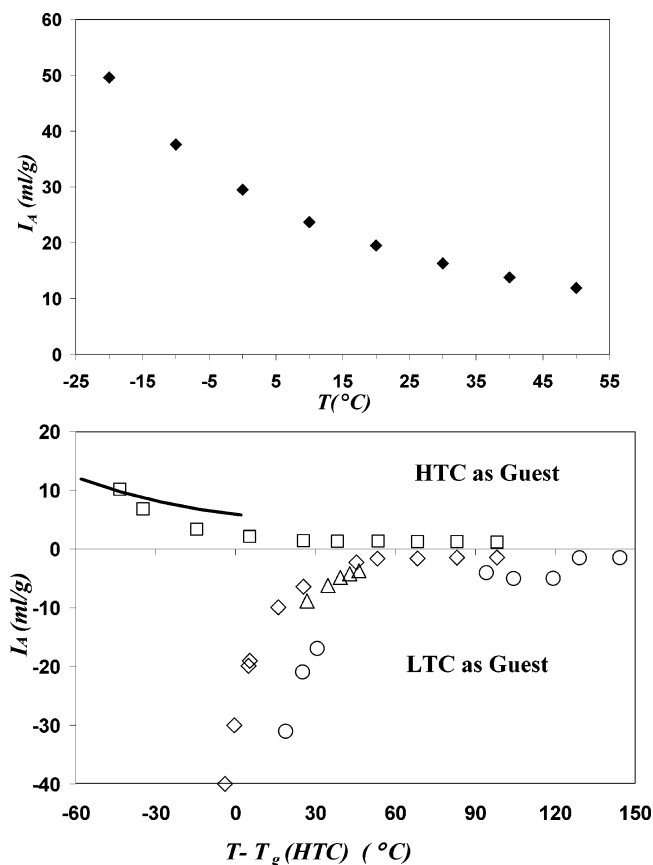


Figure 5. (a) Temperature dependence of the modification (I_A) on the segmental relaxation times of PVEE by DHN. (b) Temperature dependence of the modification (I_A) on the segmental relaxation times of host molecules by guest molecules as a function of $(T - T_g(HTC))$: Solid line — influence of DHN on PVEE, extrapolated from fit of experimental data to the VFT equation. Unfilled symbols: experimental data taken from the literature. Data from ref 2 for the influence of various polymers on the relaxation time of the small molecule Aroclor (a chlorinated biphenyl): triangles, polyisoprene; circles, 1,4-polybutadiene. Data from ref 19: squares, influence of PVE on PI; diamonds, influence of PI on PVE.

increases. That I_A approaches but does not appear to reach zero is reasonable for a miscible solution or blend, since the local environments of the components will be influenced by the other unless large-scale phase separation occurs.

Although the general effect of a guest component on the dynamics of a host can be the same for different systems, the details depend on the experimental probe and the modification can be very different for different pairs. Comparing the results from depolarized Raleigh scattering² and oscillatory electric birefringence¹⁶ experiments, high-molecular-weight PS (90k) has almost negligible effect on the DRS relaxation time of Aroclor, notwithstanding the large ΔT_g of ~ 130 K.²⁵ A comparatively larger effect was observed in mechanical relaxation spectra; however it is still orders of magnitude smaller than the effect of high-molecular-weight PS on a styrene oligomer, which has comparable τ and temperature dependences to Aroclor. This has been explained by the different extent of intermolecular coupling in the two systems.

Time Temperature Superposition (TTS). The segmental relaxation time distribution of neat PVEE is nearly independent of temperature as shown in Figure 6a, indicating that TTS is followed. The addition of DHN does not change the TTS behavior, and the normalized loss plots of the D20 and D1 mixtures are provided, respectively, in Figures 6b and 6c as

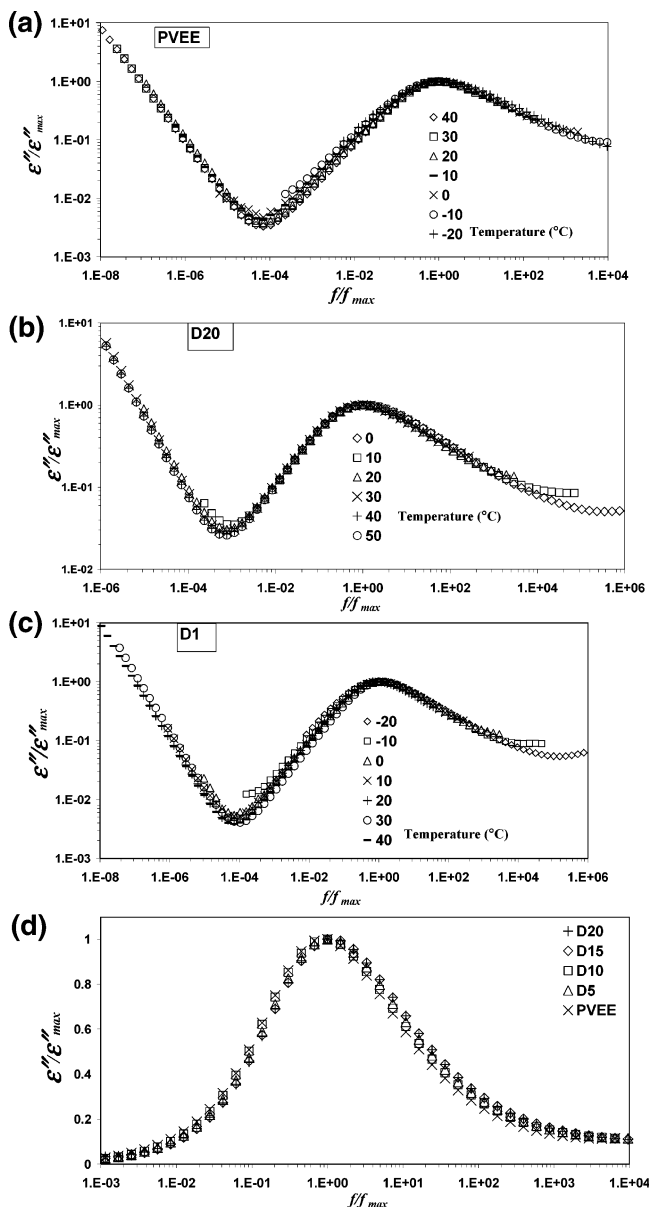


Figure 6. Normalized loss plots of the α relaxation of (a) PVEE, (b) D20 blend, (c) D1 blend. (d) Comparison of PVEE and the various DHN mixtures. In (d) the temperatures are selected to be approximately $T(100 \text{ s}) + 30 \text{ }^{\circ}\text{C}$, which are $-5, 0, 5, 10$, and $15 \text{ }^{\circ}\text{C}$ for PVEE, D5, D10, D15, and D20, respectively.

representative examples. Moreover, the DHN/PVEE mixtures have the same loss factor distribution as that of neat PVEE (Figure 6d). We fitted the data with the Havriliak-Negami (HN) equation and a dc loss contribution:²⁶

$$\epsilon(\omega) = \epsilon' - i\epsilon'' = \frac{\epsilon_0 - \epsilon_{\infty}}{(1 + (i\omega\tau)^a)^b} + \epsilon_{\infty} - i\left[\frac{\sigma}{\epsilon_v\omega}\right]^s \quad (6)$$

where ϵ_{∞} and ϵ_0 are the limiting dielectric constants at high and low frequencies, respectively ($\epsilon_0 - \epsilon_{\infty} = \Delta\epsilon$, the relaxation strength.); ω is the angular frequency; τ the characteristic relaxation time; σ the conductivity; ϵ_v the vacuum permittivity, $8.85 \times 10^{-12} \text{ F/m}$; and s characterizes the conduction process. The exponents a and b ($0 < a, b < 1$) represent the breadth and asymmetry of the relaxation, respectively, and they were found to be about 0.75 and 0.5, respectively.

For the most extensively investigated miscible polymer blend without strong intermolecular interactions, polyisoprene/poly-

(vinyl ethylene) (PI/PVE) at PVE concentrations $< 40 \text{ wt } \%$, DRS experiments unambiguously demonstrated the presence of two distinct cooperative segmental relaxation processes, with the low- and high-frequency α processes associated with PVE and PI, respectively.²⁷ At lower frequencies, the PI normal mode relaxation was observed, and it moves to higher frequencies with decreasing PI molecular weight. Assuming that the segment sizes of PVE and PI are equal to the end-to-end distance of the PI molecules when the relaxation time of the PI normal mode relaxation reaches those of the segmental relaxations of PVE and PI, Hirose et al. obtained two different length scales for the α processes of PVE and PI (0.9 and 1.8 nm, respectively).²⁷ These authors concluded that a single length scale model like that for concentration fluctuations is consequently inappropriate, and a two length scale model like the so-called self-concentration model²⁸ is more reasonable. Furthermore, recent computer simulations reveal that both intermolecular concentration fluctuation and self-concentration effects are broadly distributed, and it was argued that the effects should not be considered through their mean values only, but through their distributions.²⁹ Therefore it is reasonable to describe the component dynamics in a binary system at particular temperatures with two individual relaxation time distributions.

It has been generally accepted that the broad nonexponential loss function of a single-component glass former consists of a distribution of responses with relaxation times τ , a solid underpinning for which was obtained from the results of spectral hole-burning experiments.³⁰ This concept can be illustrated by the following expression:³¹

$$\phi(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}] = \int_0^{\infty} g(\tau) \exp[-(t/\tau)^{\beta_{\text{Intr}}}] d\tau \quad (7)$$

The first equality in eq 7 is the stretched-exponential Kohlrausch-Williams-Watts (KWW) function³² that describes the macroscopic decay function in the time domain, $\phi(t)$. In the second equation, a KWW-type relaxation with stretching parameter β_{KWW} ($0 < \beta_{\text{KWW}} < 1$) was modeled as a distribution of intrinsically nonexponential decays with exponent $\beta_{\text{Intr}} \geq \beta_{\text{KWW}}$ and probability density $g(\tau)$. The parameter β_{Intr} has been found to be close to unity for small molecules³¹ and ~ 0.85 for polymers.³³ This means that every τ corresponds to a local environment with near-exponential (Debye) relaxation behavior (i.e., β_{Intr} near unity). We surmise that this scenario is suitable for describing the local environments of each component in a binary mixture. Intermolecular interactions and self-concentration effects may influence the local environment distribution of the individual components and result in different degrees of “matching” between the dynamics of the two components. Excellent “matching” can be obtained in polymer/solvent systems with suitable intermolecular interactions.

It is possible that the DHN molecules simply follow the cooperative relaxation of PVEE segments because DHN exhibits no chain connectivity and these molecules are associated with PVEE segments through hydrogen bonding. Therefore, DHN should be distributed uniformly in the PVEE matrix, and have the same effect on the environment in all regions of the PVEE matrix. Thus the characteristic τ values of each local environment increase by equal amounts due to increased intermolecular friction, but $g(\tau)$ and β_{Intr} remain unchanged. This results in a constant shape of the loss function accompanying the higher T_g .

The loss of thermorheological simplicity for segmental³⁴ and terminal relaxations³⁵ is very common in miscible polymer

blends without strong intermolecular interactions, and the failure is also widely observed in polymer/solvent systems without strong associations. For example, for concentrated solutions of chlorinated polyethylene/bis(2-ethylhexyl) phthalate³⁶ and poly(vinyl acetate)/toluene,³ the relaxation time distributions of the solutions are significantly broader than the undiluted polymer and display a systematic temperature dependence. This implies that without intermolecular associations to facilitate close contact between the chemically different species, solvent molecules may distribute nonuniformly in the polymer matrix and produce a set of $g(\tau)$ and β_{intr} different from that of the neat polymer, and hence broaden the loss function. The effect becomes more severe at lower temperatures and TTS fails. It has also been observed that the dielectric loss of PS solutions in toluene is independent of composition and temperature at 30–70 wt % PS.³⁷ However, on the basis of the reported frequency–temperature location, the dispersion investigated in ref 37 appears to be the slow α process of the two observed for toluene/PS solutions with comparable concentrations,³⁸ where the slow and the fast α processes are associated with PS-rich and toluene-rich regions, respectively. In molecular dynamics simulations of PS/benzene mixtures, it was not possible to separate benzene molecules into tightly bound slow ones and free fast ones.³⁹ This can be rationalized by somewhat stronger association between the benzene rings of the two components in the absence of the toluene methyl group.

A single cooperative segmental relaxation has been observed for globally miscible poly(4-vinylphenol) [PVPh]–PVEE blends containing 30 to 50 wt % PVPh, whereas blends with <30% PVPh display two segmental processes.¹ For the latter behavior, the slow process was attributed to the relaxation of intermolecular hydrogen-bonded PVPh and PVEE segments, while the fast one was assigned to unassociated PVEE segments. But why do DHN/PVEE mixtures not manifest such dual segmental relaxation behavior, even when containing as little as 1 wt % DHN (see Figure 6c)? We observed the same nonstoichiometric behavior in miscible solutions of PVME with bis(4-hydroxyphenyl)-methane and 4-ethylphenol, the T_g 's of which are higher and lower than that of PVME, respectively.¹¹ The DHN molecules can be considered to transfer between different local environments with the relative motions of PVEE segments. This scenario is absent in PVPh/PVEE blends with low PVPh content because the self-concentration arising from chain connectivity restricts uniform distribution of PVPh segments at low concentrations. Only in a suitable composition range where both components of the PVPh/PVEE blends distribute uniformly with reference to one another and their segmental relaxations coupled via adequate intercomponent interactions, does a single segmental process arise. These PVPh/PVEE blends exhibit thermorheological simplicity, with a relaxation breadth that changes with composition but not with temperature.

The above evidence demonstrates that suitable intermolecular interactions and the absence of self-concentration effects can promote simple segmental relaxation behavior. However, if intermolecular associations are so strong that they “fix” a component onto certain sites, then phase separation can occur and multiple segmental relaxations result. Examples of such behavior are found in polymer electrolytes⁴⁰ and ionomers.⁴¹

dc Conductance. The loss factor increases significantly at low frequencies and high temperatures, and the slopes of log–log plots in this f/T range are near unity (Figures 6a–6c and 7). High losses under such conditions could originate from dc conduction and/or electrode polarization (EP). For EP, however,

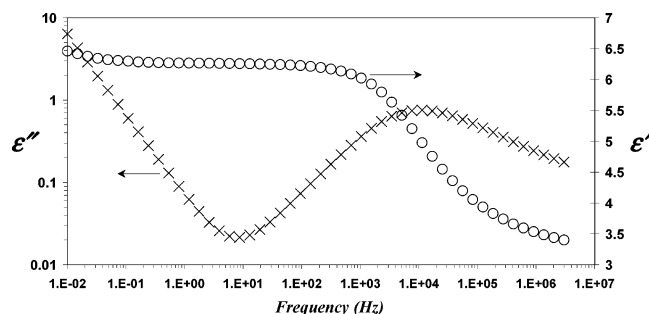


Figure 7. Dielectric ϵ'' and ϵ' as a function of frequency for the α relaxation at 30 °C for the D20 blend.

the dielectric constant is typically in the range of 10^2 – $10^{6,42}$ which is not the case here (see Figure 7). The dc conductivity has no capacitive component and thus no contribution to ϵ' . We conclude therefore that dc conductance dominates in this f/T range where ϵ' is essentially constant. It can be seen in Figure 6(a–c) that conduction losses superimpose with each other for PVEE and all DHN/PVEE mixtures under investigation, using the same shift factors as determined for the α process. This has also been observed recently in PVME/4-ethylphenol mixtures.¹¹ These results are in keeping with the observation that ion transport in most polymers is highly coupled to the segmental relaxation, and enormous efforts have been taken in an attempt to decouple ion transport and polymer segmental motion in the quest for polymer electrolytes remaining highly conductive below the T_g of the polymer matrix.⁴³

Summary

PVEE and its mixtures with up to 20 wt % DHN are amorphous, and exhibit a single DSC glass transition. T_g gradually increases with increasing DHN, but the transition width does not change within experimental uncertainty. All mixtures exhibit a single DRS α process, fitted well by the VFT equation. The segmental process gradually moves to higher temperature with increasing DHN content, while the f – T location of the sub- T_g relaxation remains invariant.

The fragility increases with DHN content, reflecting the combined contribution of both components. The similarity between the fragility behavior of miscible polymer blends and polymer/small molecule mixtures suggests that no matter whether the participating units are polymer segments or small molecules, as long as their cooperative relaxation is coupled, their chemical structures are the primary factor determining the fragility of the multicomponent system.

We calculated the modification of the DRS relaxation time of the PVEE α process by DHN. Together with published data, we observe a general feature of the influence of the guest molecules on the cooperative relaxation dynamics of the host in a miscible binary system. The influence approaches zero at ~60–100 °C above the T_g of the high T_g component, corresponding to the widely recognized critical temperature. Furthermore, this conclusion does not appear to be affected by the molecular weight of components.

The breadths of the α relaxations were found to be independent of temperature and composition. We propose that at a particular temperature both components in the mixture possess their individual distribution of local environments. DHN molecules have no contribution from chain connectivity and can closely contact PVEE segments through intermolecular hydrogen bonding. Hence, they can be uniformly distributed in the PVEE matrix, and have the same effect on every local environment of PVEE.

For all samples, the dc loss data at different temperatures can be superimposed using the same shift factors as that of the α process. This is in keeping with previous findings that ion transport in most polymers is highly coupled with the segmental relaxation.

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