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# Dynamic Homogeneity in Mixtures of Poly(vinyl methyl ether) with Low Molecular Weight Phenolic Molecules

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ABSTRACT: Dynamical homogeneity was observed in mixtures of PVME with two small molecules—4-ethylphenol [EPh] and bis(4-hydroxyphenyl)methane [BPM]—by broadband dielectric spectroscopy. TTS is valid in mixtures with EPh concentrations up to 50% and for BPM content from 2 to 30%, and all have the same segmental relaxation time distribution as neat PVME. This behavior is attributed to the strong intermolecular hydrogen bonding, increased mixing entropy, relatively small $T_g$ contrast, the absence of self-concentration effects, and reduced interchain cooperativity. However, PVME/toluene mixtures exhibit a slightly broader segmental relaxation distribution due to the absence of hydrogen bonding. We also found that strong intermolecular associations are capable of slowing down the secondary relaxation of PVME. Spatial heterogeneity is expected in mixtures with very low BPM contents based on the effect of stoichiometry, and two relaxing segments are possible in 2% BPM/PVME mixtures.

## Introduction

Recent studies of polymer dynamics have found that significant dynamic heterogeneity exists in miscible binary blends with large $T_g$ contrast ($\Delta T_g$) and without strong intermolecular interactions.[1−21] The component polymers may relax individually with a significant difference in their segmental relaxation rates. For example, in the blend of poly(methyl methacrylate) and poly(ethylene oxide) [PMMA/PEO] with PEO content ≤ 30%, Ediger and co-workers reported that the segmental relaxation of PEO is 12 decades faster than that of PMMA at the $T_g$ of the blend.[1] Similar behavior has also been observed in polystyrene/poly(vinyl methyl ether) [PS/PVME],[2−8] PVME/poly(2-chlorostyrene) [P2CS],[9] and polyisoprene/poly(vinylethylene) [PI/PVE] blends.[10−19] The dynamical heterogeneity has mainly been interpreted by means of concentration fluctuations,[22,23] intrinsic mobility differences[9,19] and, more recently, self-concentration effects.[24]

However, the dynamic heterogeneity can be reduced or even eliminated by introducing intermolecular interactions. We recently investigated the relaxation behavior of a number of polymer blends with strong intermolecular hydrogen bonding using broadband dielectric relaxation spectroscopy (DRS), e.g., blends of poly(4-vinylphenol) [PVPh] with poly(vinyl ethyl ether) [PVEE] and poly(vinyl methyl ether) [PVME].[25−29] Although the blend $\Delta T_g$s are very large (≥150 K), we found that concentration fluctuations can be damped and the components' segmental relaxations can be coupled, if all relaxing segments are associated through intermolecular hydrogen bonds. The hydrogen bonding serves as "stickers", and the blend can be considered a transient network. For PVEE/PVPh blends with PVPh concentration < 30%, however, two segmental relaxation processes were observed. This was rationalized by considering the stoichiometry for hydrogen bonding: the slow process was attributed to the relaxation of hydrogen-bonded PVPh−PVEE segments and the fast one to the unassociated low-$T_g$ component.[27]

As an extension of previous studies, we present our dielectric results on mixtures of PVME with two model phenolic molecules: 4-ethylphenol [EPh] and bis(4-hydroxyphenyl)methane [BPM]. While EPh has only one hydroxyl group per molecule, BPM has two −OH and can perhaps serve as a transient "cross-linking agent". These two small molecules have chemical structures similar to that of the PVPh repeat unit, and the present results will provide useful insight into our understanding of the more complex dynamics of PVME/PVPh blends, particularly the role of chain connectivity. For comparison, mixtures of PVME with toluene were also explored in order to examine the effect of intermolecular hydrogen bonding. Our results will also be compared to those for dilute polymer solutions and plasticized polymers.

The investigation of the rotation and diffusion of small molecules in polymer materials has practical importance for a variety of applications, e.g., packaging (diffusion of gas and water molecules), rechargeable ionic batteries with polymer electrolytes (motion of ions in cooperation with PEO segmental relaxations), controlled drug release, and doped electric/optic polymers (frozen orientation of the guest molecules in the glassy host polymers). Understanding how guest molecules relax in the host as well as how they can modify relaxations of the host polymers will provide guidance for future materials design. The present systematic study will particularly shed light on the influence of intermolecular hydrogen bonding.

## Experimental Section

**A. Materials and Sample Preparation.** PVME was purchased from Scientific Polymer Products Inc. and has $M_w = 46\,000$ and $M_n = 8400$, as determined by gel permeation chromatography using tetrahydrofuran as the mobile phase and narrow molecular weight distribution polystyrene standards. EPh and BPM are products of Aldrich and used without further purification. Both phenols are highly crystalline molecules, with melting temperatures of 45 and 159 °C for EPh and BPM, respectively.

PVME/EPh and PVME/BPM mixtures were prepared by solution casting, and acetone was used as the solvent to facilitate later solvent removal. After evaporating most of the

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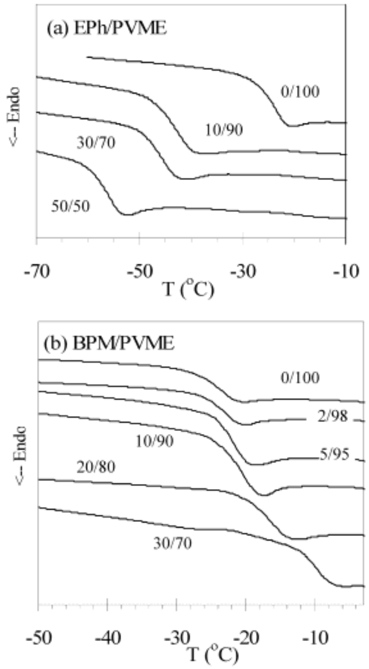

**Figure 1.** DSC thermograms of PVME mixtures with (a) EPh and (b) BPM: second heating run, heating rate = 10 K/min.

solvent in a mixing vessel, the viscous solution was poured onto an electrode and held in a desiccator for 24 h. Then the samples were placed into a vacuum oven for another 72 h: at room temperature for PVME/EPh and at 60 °C for PVME/BPM mixtures. The different temperatures were selected to prevent the loss of small molecules in a vacuum. Finally, another electrode was placed on top of the sample. A polypropylene spacer was used to control the sample thickness, which is around 250 $\mu$m thick. Both electrodes are made from gold-sputtered stainless steel with a diameter of 3 cm. Mixtures with EPh weight concentration of 10%, 30%, and 50% and with 2%, 5%, 10%, 20%, and 30% BPM were studied. Solutions of PVME with 10% and 20% toluene were prepared by directly depositing the appropriate amount of toluene into PVME.

Samples for DSC analysis were taken directly from the solvent-evaporated DRS mixtures immediately before the dielectric experiment.

**B. Characterization.** Dielectric spectra $\epsilon^*(f,T)$ were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency domain [0.01 Hz−10 MHz], on cooling from $\sim T_g + 80$ K to −160 °C. Temperature was controlled by a Novocontrol Quatro Cryosystem, which uses $N_2$ to heat and cool the sample and has a stability of ±0.1 K.

DSC experiments were performed using a TA Q100 instrument. The samples were first heated to 50 K above the expected $T_g$, held for 3 min, and then cooled at a rate of 20 K/min. After soaking at −90 °C for 5 min, the sample was heated again at a rate of 10 K/min. $T_g$ was taken as the midpoint of the heat capacity change in the second heating run.

## Results

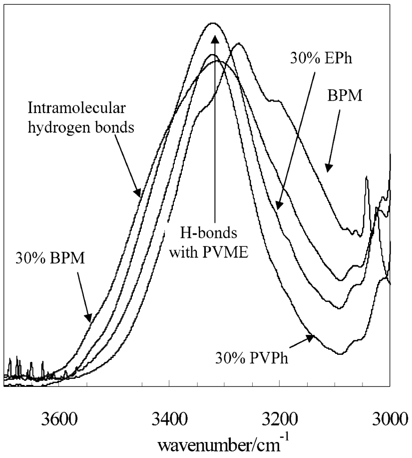

**Figure 2.** IR spectra of neat BPM and selected mixtures at room temperature. The intensities of these spectra have been adjusted for comparison.

**A. Miscibility of the Mixtures.** Unlike polymer−polymer blends, miscibility between polymers and small molecules can be readily achieved due to the significant combinatorial entropy contribution to the free energy of mixing. For PVME/EPh and PVME/BPM mixtures, the miscibility is additionally favored by strong intermolecular hydrogen bonding. Miscibility was confirmed by DSC studies (Figure 1), in which a single $T_g$ was observed for each mixture. Moreover, the glass transitions are relatively narrow with a width comparable to neat PVME (<10 K), in contrast to the rather broad transitions observed for many miscible polymer blends (∼30 K). The different behavior can be attributed to the improved homogeneity of the former. It is important to emphasize that there is no evidence for crystalline EPh or BPM in any of the mixtures analyzed in the present study.

$T_g$'s of the PVME/EPh mixtures gradually decrease with increasing EPh concentration. Although EPh is a highly crystallizable molecule, we found a $T_g$ of −67 °C after quenching from the melt to liquid nitrogen temperature. For PVME/BPM, however, the $T_g$ exhibits an increase with BPM concentration. BPM crystallizes very rapidly, and no amorphous component was detected even after quenching from the melt. Nonetheless, we speculate that the $T_g$ of amorphous BPM should be higher than that of PVME, in light of the general relationship, $T_m \approx 1.3 \times T_g$, that has been found for small organic molecules that can be obtained in both the crystalline and amorphous states.[30] This leads to an estimated $T_g$ of about 59 °C for BPM, ∼87 °C higher than $T_g$ (PVME). Part of the increase in $T_g$ in PVME/BPM may also be attributed to the associative nature of the BPM molecules, whose two hydroxyl groups are capable of forming a transient network with PVME, whereas EPh can only increase the fractional free volume and decreases interchain interactions in PVME.

Since the chemical structures of EPh and BPM are similar to that of the PVPh repeat unit, the −OH groups of both phenolic model compounds are expected to form hydrogen bonds with proton acceptors like PVME. Moreover, the strength of these hydrogen bonds should be close to that between PVPh and PVME. This is confirmed by their infrared spectra (Figure 2). The main band in the spectral region shown in Figure 2 arises from hydroxyl groups that are hydrogen bonded with PVME. This band is located around 3325 cm$^{-1}$ for mixtures containing EPh, BPM, or PVPh. For 30% proton donor, effectively all EPh are hydrogen bonded with PVME, whereas intramolecular hydrogen bonds emerge in BPM and PVPh. The fraction of intramolecular hydrogen bonding in the latter, however, is relatively small as compared with that of intermolecular associations, at least for the compositions used in the present study. It should be noted that the three bands in this region of the neat BPM spectrum result from its crystalline nature, in which the highly ordered structure leads to very strong hydrogen bonding.

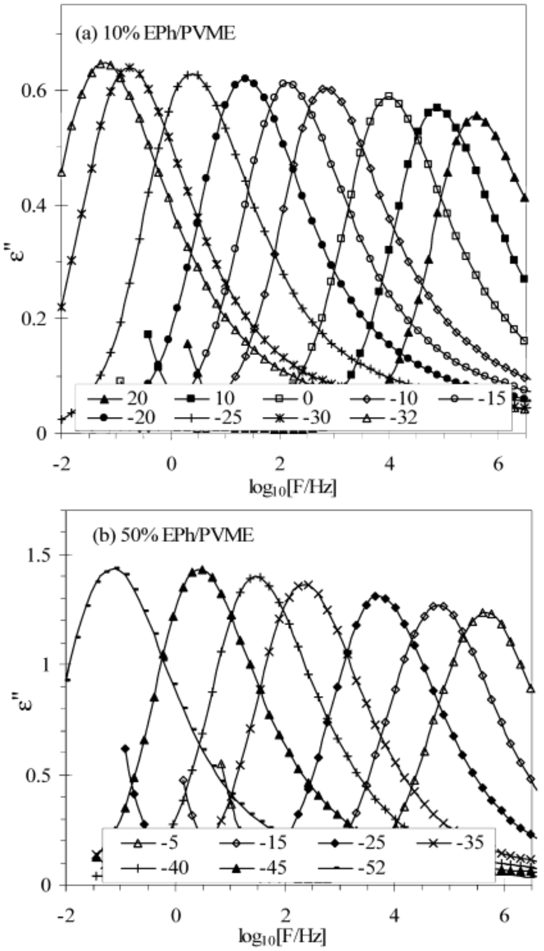

**Figure 3.** DRS loss spectra of PVME mixtures with (a) 10% and (b) 50% EPh. The labels inside each figure provide corresponding temperatures in °C.

**B. Dielectric Segmental Relaxation of PVME/EPh Mixtures.** Consistent with the DSC results, a single segmental relaxation process is observed in the loss spectra of all three PVME/EPh mixtures investigated (Figure 3). The segmental relaxation occurs above $T_g$ and involves the cooperative relaxation of a few repeat units. This relaxation becomes faster with increasing temperature for a particular mixture or with increasing EPh concentration at constant temperature.

It has been found that the segmental relaxation of PVME has essentially the same relaxation time distribution at different temperatures, with a full width at half-maximum of about 2.5 decades, suggesting that the time−temperature superposition (TTS) principle is valid for this process.[29] This behavior is observed for all three PVME/EPh mixtures. Figure 4 contains the dielectric master curve of the mixture with 30% EPh. TTS works well for this mixture, with a performance comparable to neat PVME, and also for mixtures with 10% and 20% EPh (master curves not shown). The dc conduction, observed at low frequencies, also reduces to a single master curve with the same shifting parameters used for the segmental relaxations. This suggests that the impurity ion motion in the mixtures is completely coupled with the segmental relaxation of the host polymer through hopping from one segment to the next. We do observe slight broadening at high frequencies for both neat PVME and the mixtures. This can be attributed to the low-frequency tail of the $\beta$ process of PVME, whose relaxation time has different temperature dependence from that of the α process.

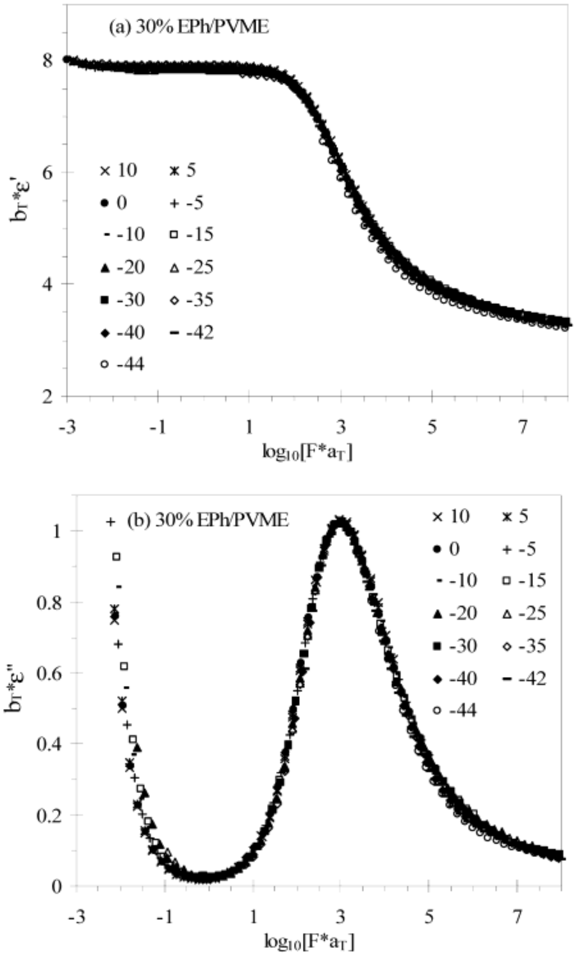

**Figure 4.** Dielectric master curve of the 30/70 EPh/PVME mixture. The labels inside each figure provide corresponding temperatures in °C. The data at the reference temperature, −20 °C, are shown in filled triangles. Both $\epsilon'$ and $\epsilon''$ are shifted with the same set of shift factors.

The width of the segmental relaxation time distribution is invariant with composition (Figure 5). This indicates unusual dynamical *homogeneity* of the mixtures, in contrast with the significant broadening (with temperature and composition) observed for many miscible polymer blends. One immediate conclusion from this behavior is that concentration fluctuations are damped in the PVME/EPh mixtures.

The dielectric relaxation strength ($\Delta\epsilon$), defined as the area below the $\epsilon'' \sim \ln(f)$ spectrum or the difference between the relaxed and unrelaxed dielectric constants, increases significantly with EPh concentration. Figure 6 summarizes $\Delta\epsilon$ for different mixtures at different normalized temperatures, obtained by fitting the dielectric loss spectra with the phenomenological Havriliak−Negami (HN) equation.[31] $\Delta\epsilon$ decreases with increasing temperature as a result of reduced cooperativity and enhanced randomization from higher thermal energy.

The considerable increase in $\Delta\epsilon$ with EPh concentration demonstrates that EPh contributes to the observed relaxation. That is, guest EPh molecules follow the segmental relaxation of PVME, although they have modified the latter through plasticization at the same time. This conclusion has practical significance, considering

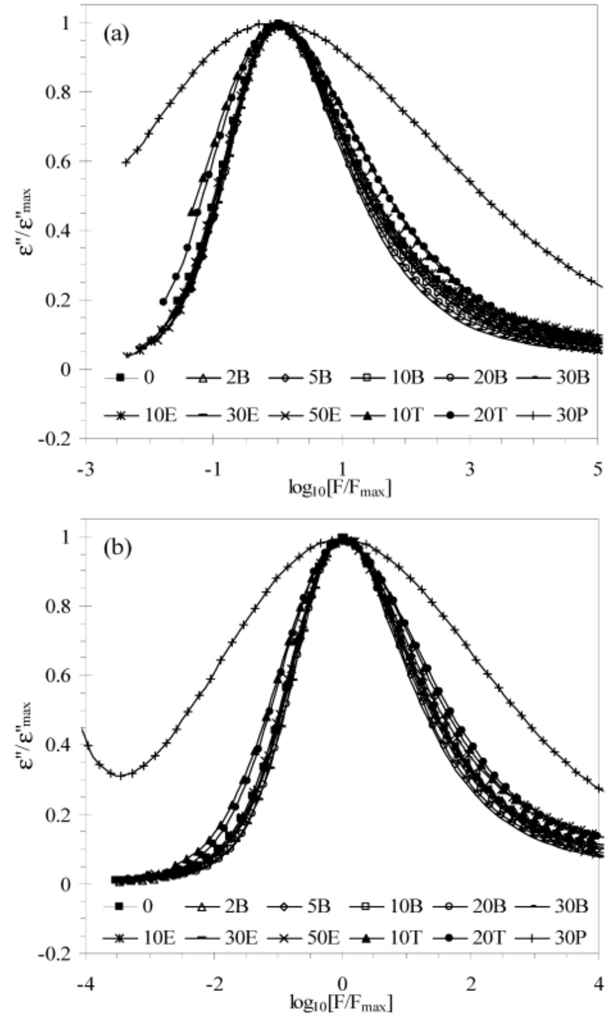

**Figure 5.** Comparison of the dielectric loss spectra of different mixtures (at approximately the same normalized temperatures) with the original peak maximum located at (a) 1 Hz and (b) 50 Hz. Data of 30/70 PVPh/PVME from ref 29. The number in the label refers to the percentage of the small molecules by weight; "E", "B", "T", and "P" refer to mixtures with EPh, BPM, toluene, and PVPh, respectively.

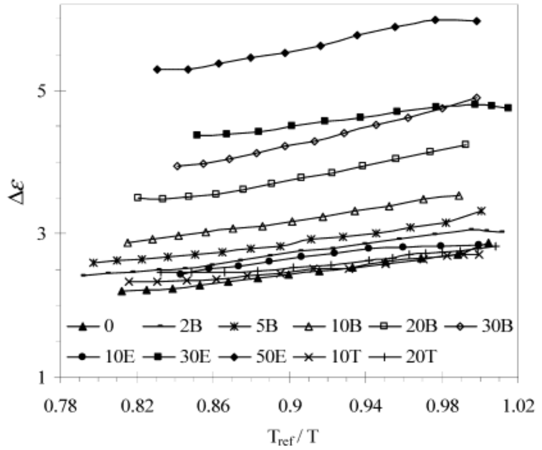

**Figure 6.** Dielectric segmental relaxation strengths ($\Delta\epsilon$) of different mixtures at normalized temperatures. $T_{\mathrm{ref}}$ is defined as the temperature at which $\tau_{\max} = 1$ s, as shown in Table 1. Labels have the same meaning as in Figure 5.

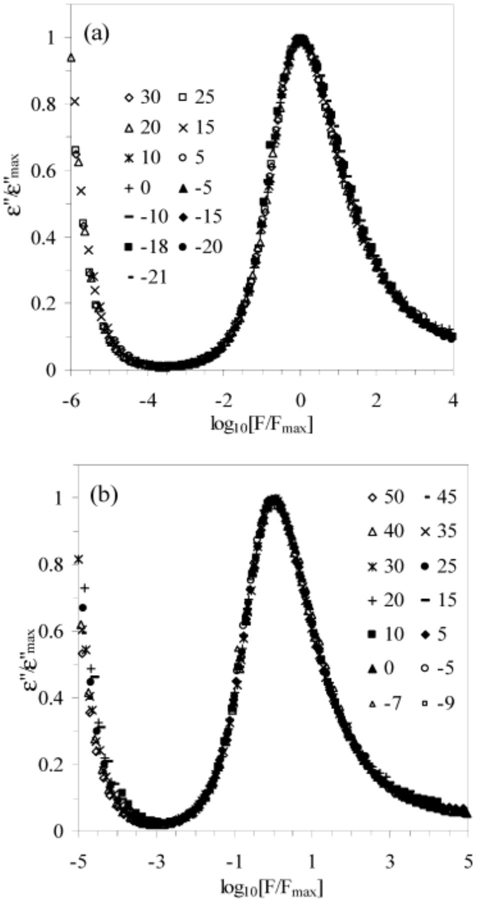

**Figure 7.** DRS loss spectra of PVME mixtures with (a) 10% and (b) 30% BPM. The labels in each figure give corresponding temperatures in $^{o}$C. All spectra have been normalized by the corresponding $\epsilon''_{\max}$ and $F_{\max}$.

that the rotational reorientation of small molecules (gases, drugs, water molecules, and ions) is coordinated with the segmental relaxation of the host polymer, and the relaxation of oriented electrically or optically active guest molecules can be retarded by controlling the segmental relaxation of the host polymers.

**C. Dielectric Segmental Relaxation of PVME/BPM Mixtures.** PVME/BPM mixtures have similar segmental relaxation behavior as that observed for PVME/EPh, except that the segmental relaxation becomes slower with increasing BPM content as a result of increased $T_g$. The segmental relaxation time distribution of PVME/BPM is also independent of temperature (Figure 7) and composition (Figure 5), with almost the same breadth as neat PVME. Therefore, TTS is valid for all PVME/BPM mixtures investigated. Their dielectric relaxation strengths also increase with BPM concentration (Figure 6), from ∼2.7 for PVME to ∼4.7 for the mixture with 30% BPM.

**D. Segmental Relaxation of PVME/Toluene Mixtures.** Since the dipole moment of toluene (∼0.4 D) is much smaller than those of PVME (∼1.22 D), EPh (∼1.61 D), and BPM (∼1.16 D),[32] $\Delta\epsilon$ for PVME/toluene mixtures are slightly lower than that of neat PVME. As a good solvent for PVME, toluene decreases the $T_g$ significantly and shifts the segmental relaxation to higher frequency. TTS works well in the two toluene mixtures studied (Figure 8), but the dielectric loss peaks are broadened slightly compared with neat PVME and the other two mixtures containing intermolecular hydrogen bonds (Figure 5).

The segmental relaxation process in glass-formers is correlated with the glass transition behavior. Its tem-

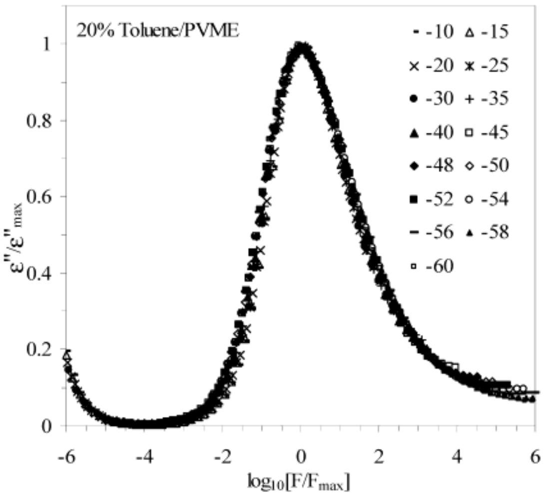

**Figure 8.** DRS loss spectra of PVME mixtures with 20% toluene. The labels provide the corresponding temperatures in °C. All spectra have been normalized by the corresponding $\epsilon''_{\max}$ and $F_{\max}$.

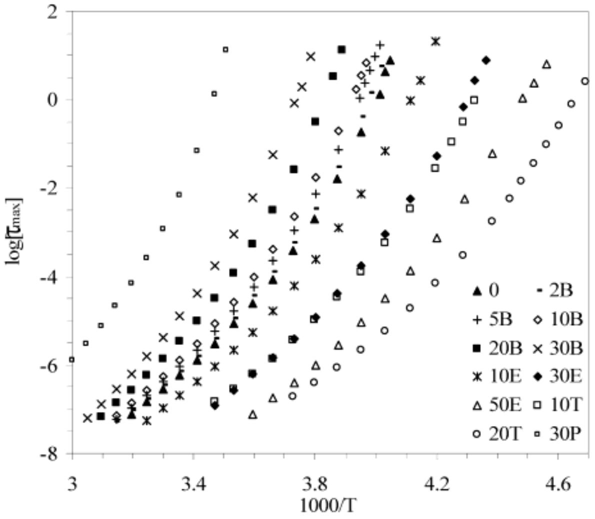

**Figure 9.** VFT plot of the segmental relaxation process in all mixtures. Labels have the same meaning as in Figure 5.

perature dependence is generally non-Arrhenius and should be described by the well-known Vogel−Fulcher−Tammann (VFT) equation:[33]

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{1}$$

in which $\tau$ is the segmental relaxation time and $\tau_0$ a prefactor correlated to the time scale at which the molecules are attempting to overcome some energy barrier. $B$ is a parameter related to the strength for glass-forming. $T_0$ is a temperature below $T_g$ and at which the segments are frozen. Figure 9 contains the VFT plot of all mixtures, with $\tau_{\max}$ determined by fitting the original dielectric loss spectra with the HN function. It is clear that the curves are shifted to higher temperature for mixtures with higher $T_g$s. The fitted VFT parameters are provided in Table 1.

**E. Dielectric Secondary Relaxations.** The secondary $\beta$ relaxation of PVME involves the rotation of the $-OCH_3$ side groups around C−O bonds linked to the chain backbone. Since the C−O bond is very flexible, this process occurs at very low temperatures, e.g., below −100 °C in the available frequency window. After introducing small molecules, $\epsilon''_{\max}$ becomes smaller with increasing diluent content due to the consequent lower PVME concentration (Figure 10). The relaxation time distribution broadens toward low frequencies in mixtures with EPh and BPM as well as blends with PVPh, and the fraction of the relatively slow process becomes larger at lower PVME concentrations. The existence of some slowly relaxing units is perhaps a result of the intermolecular hydrogen bonding with the EPh, BPM, or PVPh, as such interactions may increase the energy barrier for $-OCH_3$ rotation. The suppression of the host polymer's $\beta$ relaxation was also observed in our previous study of azo dye−PMMA mixtures, which also involves intermolecular hydrogen bonding between the guest molecules and side groups of the host.[34] One additional feature of the $\beta$ relaxation is that the population of the more slowly relaxing species becomes stronger in the order PVPh < BPM < EPh, at 30% concentration by weight, although the hydroxyl group concentrations are almost the same in each. This can be readily understood by considering their abilities to form intermolecular hydrogen bonds with PVME, which follows the same order due to steric constraints or intramolecular screening.[35]

The ability of hydrogen bonding to retard local relaxations is further confirmed by comparing with the results of PVME/PS[3] and PI/PVE[17] blends. The strengths of the $\beta$ relaxations of the component polymers were observed to be approximately proportional to the concentration of the corresponding polymer, indicating unmodified local dynamics. These results are reasonable considering that the interactions between PVME and PS, or between PI and PVE, are very weak, with polymer−polymer interaction parameters ($\chi$) $\approx -0.001$ to $-0.01$. It should be noted however that hydrogen bonding does not necessarily lead to retardation; this depends on hydrogen bond strength and the mechanism of the process of interest. For example, we found that the $\beta$ relaxation of poly(ethyl methacrylate) (PEMA) remains essentially unchanged in blends with PVPh.[25]

For the mixture with 20% toluene, the PVME $\beta$ relaxation is shifted slightly to higher frequency; i.e., the side group rotation of PVME becomes somewhat faster after mixing with toluene. This is perhaps a result of the absence of strong intermolecular interactions, as well as reduced density resulting from mixing, which releases some steric constraints.

## Discussion

**A. Dynamical Homogeneity.** As discussed in the Introduction, significant dynamical heterogeneity has been observed in many miscible polymer blends. The breadth of the segmental relaxation reflects the distribution of segmental mobility, which is highly influenced by the environment. As shown in Figure 5, although strong intermolecular hydrogen bonding is believed to be capable of coupling components' segmental relaxations, the relaxation time distribution is still very broad, ~5 decades in 30/70 PVME/PVPh blend at ~$T_g$ + 20 K,[29] compared to ~2.5 decades for the mixtures with EPh or BPM at any composition and temperature.

The dynamical homogeneity in these two mixtures can be understood by considering the difference between PVPh and these two small molecules, that is, the different $T_g$'s and thus different $\Delta T_g$'s of the mixtures and the degree of polymerization ($N$): $N \gg 1$ for PVPh,

**Table 1. Comparison of Reference Temperatures and Fragilities**

| EPh/PVME | 0/100 | 10/90 | 30/70 | 50/50 |
|---|---|---|---|---|
| $\tau_0$ (s) | $4.2 \times 10^{-13}$ | $5.3 \times 10^{-14}$ | $1.47 \times 10^{-14}$ | $4.5 \times 10^{-15}$ |
| $T_0$ (K) | 203 | 189 | 177 | 166 |
| $B$ (eV) | 0.116 | 0.143 | 0.152 | 0.161 |
| $T_{\mathrm{ref}}$ (K) | 250 | 243 | 233 | 223 |
| $F$ | 66 | 60 | 58 | 57 |

| BPM/PVME | 2/98 | 5/95 | 10/90 | 20/80 | 30/70 |
|---|---|---|---|---|---|
| $\tau_0$ (s) | $4.1 \times 10^{-13}$ | $3.8 \times 10^{-13}$ | $9.0 \times 10^{-14}$ | $1.4 \times 10^{-12}$ | $1.4 \times 10^{-12}$ |
| $T_0$ (K) | 205 | 206 | 203 | 210 | 214 |
| $B$ (eV) | 0.115 | 0.116 | 0.134 | 0.131 | 0.145 |
| $T_{\mathrm{ref}}$ (K) | 252 | 254 | 255 | 262 | 268 |
| $F$ | 67 | 67 | 64 | 67 | 67 |

| PVPh/PVME[a] | 30/70 | 50/50 | toluene /PVME | 10/90 | 20/80 |
|---|---|---|---|---|---|
| $\tau_0$ (s) | $3.5 \times 10^{-12}$ | $1.4 \times 10^{-12}$ | | $9.0 \times 10^{-14}$ | $8.1 \times 10^{-14}$ |
| $T_0$ (K) | 247 | 286 | | 179 | 164 |
| $B$ (eV) | 0.0956 | 0.0940 | | 0.134 | 0.131 |
| $T_{\mathrm{ref}}$ (K) | 289 | 326 | | 231 | 215 |
| $F$ | 79 | 97 | | 58 | 56 |

[a] Data from ref 29.

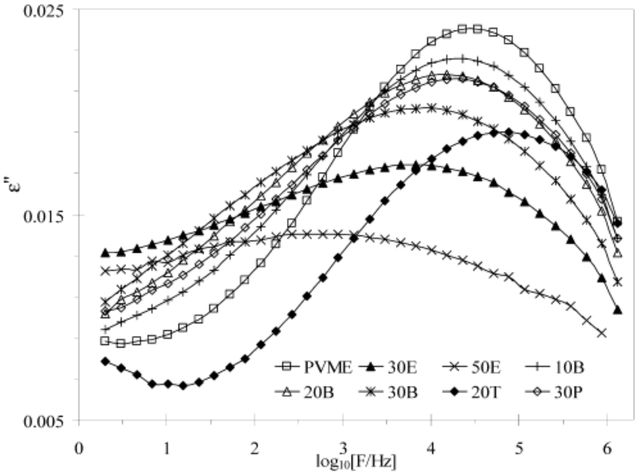

**Figure 10.** Secondary relaxation process of PVME in the mixtures at −120 °C. Labels have the same meaning as in Figure 4. Data for the 30/70 PVPh/PVME blend are from ref 29.

$N = 1$ for EPh, and $N = 2$ for BPM. The effects of these differences on the mixtures' dynamics will be discussed in detail by considering their specific influence on the application of the primary models used to interpret the dynamical heterogeneity in polymer blends.

First, $\Delta T_g$ plays a significant role in establishing dynamical heterogeneity. PVPh and PVME have a $\Delta T_g$ of ~195 K, indicating a very large mobility difference between them. On the other hand, $\Delta T_g \approx 45$ K for PVME/EPh and ~87 K for BPM/PVME: both are considerably smaller compared to that of the polymer blend. Consequently, the mobility difference between PVME and EPh or BPM is so small that it can be readily reduced through sharing identical free volume and environment in the mixture, whereas mixing itself is not sufficiently strong to completely eliminate the large mobility difference between PVPh and PVME, although the difference has been significantly diminished.

Second, polymer−small molecule mixtures are capable of greater spatial homogeneity than the corresponding polymer blends. In the latter, chain connectivity prevents a statistically random distribution of the different components' segments. As predicted by the self-concentration model by Lodge and McLeish,[24] the two components may "feel" distinctly different local compositions, which are richer in themselves compared with the bulk composition, and therefore have different "effective" $T_g$'s and segmental relaxation times in the blend. An immediate result of this is the broadening of both the glass transition and the segmental relaxation time distribution. Small molecules, on the other hand, can be randomly distributed in the polymer matrix without preference, if we assume that the intramolecular hydrogen bonding strength is comparable to that of the intermolecular association. This leads to a more spatially homogeneous system, and dynamic homogeneity is a natural consequence. However, spatial heterogeneity can be introduced if the concentration of small molecules is too low or too high, as discussed later.

Finally, concentration fluctuations [CF] can be damped in the mixtures. CF are intrinsic to polymer blends and have been proposed by Fisher et al. and modified by Kumar et al. to interpret broadened segmental relaxation time distributions. Different local nanodomains (or cooperatively rearranging regions, CRR) can have different concentrations due to thermal fluctuations, and the probability $P_{\mathrm{dynamic}}(\phi)$ of finding a concentration $\phi$, other than the bulk $\phi_0$, follows a Gaussian distribution:[2,23,36]

$$P_{\mathrm{dynamic}}(\phi) \sim \exp\left[\frac{-(\phi-\phi_0)^2 b^2 d^3 T_0^{\,2}}{24\xi^2\phi_0(1-\phi_0)(T-T_0)^2}\right] \qquad (2)$$

in which $b$ is the monomer size, $d$ a material-specific dimensionless constant, and $T_0$ the Vogel temperature. The correlation length $\xi$ can be estimated by

$$\frac{\xi}{b} = \left(12\left[-2\chi\phi_0(1-\phi_0) + \frac{1}{2N_1} + \frac{1}{2N_2}\right]\right)^{-1/2} \qquad (3)$$

where $N_1$ and $N_2$ are the degrees of polymerization of components 1 and 2, respectively.

On the basis of eq 3, decreasing the degree of polymerization leads to a smaller correlation length, which may be smaller than the segmental size. Moreover, the probability $P_{\mathrm{dynamic}}(\phi)$ is also significantly decreased for smaller correlation length $\xi$, indicating less significant concentration fluctuations (eq 2).[36] This has been confirmed in a study of molecular weight effects on the dynamics of PI/PVE blends. TTS will fail if there are significant concentration fluctuations since the degree of CF changes with temperature. For a 40/60 PI($M_w = 75\,000$)/PVE($M_w = 204\,000$) blend, it is not possible to construct a master curve from oscillatory shear data, as a result of concentration fluctuations.[37] However, for a 50/50 blend consisting of oligomers (i.e., $M_w = 770$ for PI and 2400 for PVE) Pathak found that TTS worked reasonably well.[36] It follows that the same result can be achieved when one small molecule component is used, which reduces $N_2 \sim 1$, if there is no strong repulsion between the polymer and the small molecule. This is true for PVME/toluene since toluene is a good solvent for PVME. This means that the stability of the mixed solution, as compared to the phase-separated state, is very high, and therefore thermal fluctuations are unable to induce CF.

Additionally, the intermolecular hydrogen bonding between PVME and EPh or BPM leads to a more negative effective $\chi$, and this has a similar effect on suppressing CF as that of decreasing the degree of polymerization. Reducing $\chi$ from $-0.01$ (a typical value for PVME/PS blends) to $-0.6$ has a similar effect on the correlation length $\xi$ as decreasing $N_2$ from ~200 (i.e., for PVPh used in the PVME blend) to 2 (for BPM) for a 30% mixture. It should be noted that the above argument also suggests that CF are damped in PVME/PVPh blends as well.[29] It follows that the observed broad relaxation time distribution in PVME/PVPh is likely a result of their intrinsic mobility differences and chain-connectivity effects.

The dynamical homogeneity of PVME/small molecule mixtures can also be explained by considering the influence of the small molecules on interchain cooperativity. In PVPh/PVME blends, relaxation of one unit requires cooperative rearrangement of its nearest-neighbor units, which include some belonging to the other component. The rearrangement of the latter units transfers the cooperativity to other polymer chains through chemical bonds, which more or less has a “magnification” effect. That is, relaxation of one repeat unit will “feel” a variety of environments and segments belonging to both components. On the other hand, in mixtures of polymers with small molecules, the cooperativity will be weakened at the small molecule. That is, one CRR involves only one polymer chain segment and its neighboring small molecules. We noted that the unavailability of free volume and topological constraint are the primary reason for cooperative relaxation, but we emphasize that small molecules can effectively reduce polymer interchain cooperativity and promote dynamical homogeneity, leading to a narrow relaxation time distribution. The correlation between stronger interchain cooperativity and breadth of the α process has been found for many homopolymers.[38]

The reduced cooperativity in the mixtures can be confirmed by evaluating their fragilities. Fragility is defined as

$$F = \frac{\mathrm{d} \log \tau_{\max}}{\mathrm{d} T_{\mathrm{ref}}/T}\Big|_{T=T_{\mathrm{ref}}}$$

and it reflects the temperature sensitivity of the segmental relaxation time:[39,40] higher fragility has been correlated with stronger intermolecular coupling or larger segmental size.[41] $T_{\mathrm{ref}}$ is a reference temperature and usually defined as $T$ ($\tau_{\max} = 1$ s). The calculated fragilities and $T_{\mathrm{ref}}$'s are collected in Table 1. A significant increase in fragility was observed in PVPh/PVME blends: from 66 for PVME to 79 for the blend with 30% PVPh and to 87 for the 50/50 blend, consistent with the observation of a very broad segmental relaxation time distribution. For mixtures with low molecular weight phenolic molecules, however, the fragility either decreases (for EPh) or remains unchanged (for BPM) compared with neat PVME, indicating weakened cooperativity. This explains the observation of dynamic homogeneity comparable to that of the homopolymer PVME.

**B. Spatial Heterogeneity.** Whereas the dynamical homogeneity in mixtures with EPh (or BPM) concentration higher than 10% can be interpreted by considering the strong intermolecular hydrogen bonding and large mixing entropy, for mixtures with low BPM concentrations (e.g., 2% or 5%) one would predict some heterogeneity based on a simple stoichiometric argument. In the 2/98 mixture, for example, the molar ratio of the proton donor to acceptor is only 1/72. This means that only a very small portion of PVME repeat units are hydrogen bonded with EPh, and two types of relaxing segments with different relaxation times would be expected. That is, two segmental relaxation processes are predicted: a slow one from the relaxation of hydrogen-bonded PVME and BPM (since BPM increases the mixture's $T_g$) and a fast one from unassociated PVME segments. At first glance, there appears to be single dielectric loss peak for both the 2 and 5% BPM mixtures above their $T_g$'s, although this does not necessarily imply that there is only one kind of relaxing segment. We fit the segmental loss peak of the 2% BPM/PVME mixture at −20 °C with two HN functions by assuming that the unassociated PVME segments in the mixture follow the same dynamics as those in the homopolymer at the same temperature. Two segmental relaxation processes with $\Delta\epsilon(\text{slow})/\Delta\epsilon(\text{fast}) \approx 4/1$ are resolved. However, the relaxation time of the slow process is only ~2.5 times faster than that of PVME; this suggests that the modification of PVME dynamics by BPM is not so substantial at this composition.

Because the $T_g$ of PVME can be increased significantly upon introducing BPM, BPM should conceivably be able to modify the dynamics of PVME (slowing down its relaxation), and the existence of two kinds of relaxing segments in the mixtures is a natural consequence. If there is only one kind of independently relaxing segment in the mixture with 2% BPM, we estimate that it would include at least ~78 polymer repeat units plus one BPM molecule on average, much larger than the usually accepted size of 1−3 nm for CRRs, as determined using different techniques. Consequently, the results are in keeping with the idea that dynamic heterogeneity is possible in mixtures with very low BPM compositions, although it cannot be clearly observed using DRS.

The issue of possible spatial heterogeneity has been reviewed by Lodge for dilute polymer solutions, in which attention was focused on how a small concentration of polymer chains influence the dynamics of the solvent.[42] Two populations of solvent molecules were observed in dilute PS/Aroclor 1248 solutions with PS concentration $< 0.146$ g/cm$^3$ by depolarized Rayleigh scattering: one mobile and the other modified by the polymer, at temperatures well above their $T_g$'s.[43] However, solvent dynamics were found to be unchanged at temperatures approaching the corresponding $T_g$ in the same mixture and polybutadiene [PB]/Aroclor 1248 dilute solutions.[44] We speculate that the CRR size at high temperatures is very small so that PS can only modify the dynamics of a portion of Aroclor molecules, whereas around $T_g$, the CRR size of PS or PB is very large and all solvent molecules are within the CRR of PS or PB. In a computer simulation, Lodge concluded that at 0.02 PS volume fraction about half of the Aroclor 1248 molecules are within 5 solvent diameters of polymer chain.[42] Therefore, the answer to whether two solvent populations exist or not depends on the length scale over which the polymer chain can exert its influence on the neighboring solvent dynamics.

The same argument also applies to the current issue. Whether the resolution of two kinds of segments in the mixture with 2% BPM is merely a curve fitting artifact or carries some physical significance requires further support, particularly information on the dynamics of the individual components. For example, the relaxation of PVME in the mixture can be selectively measured with neutron scattering or NMR after deuteration, and comparison of the dynamics of PVME in the mixture and its neat state can reveal any dynamic heterogeneity.

Rizos and Ngai found that the concentration fluctuation-induced dynamic heterogeneity can be partially averaged out if the radius of gyration ($R_g$) of the polymer is larger than the CRR size of the solvent.[45] In a dielectric and photon correlation spectroscopy study of the dynamics of low molecular weight Aroclor modified by PI (or 1,4-polybutadiene) having different molecular weights, they observed that a higher $M_w$ polymer leads to less temperature-sensitive dynamics of Aroclor. The change from "low $M_w$" to "high $M_w$" behavior was found to occur in a stepwise fashion when the $R_g$ is $\sim$1.5 nm, corresponding to $M_w \sim 2500$. This argument, however, is based on solutions with polymer concentrations less than 20% and focuses on the dynamics of solvent; therefore, it does not apply to the current study of polymer dynamics modified by relatively low solvent concentration.

Finally, it should be noted that studies of certain plasticized polymers (e.g., poly(vinyl acetate) and poly(vinyl chloride)) reveal two dielectric relaxation processes above the corresponding $T_g$ when plasticizer concentrations are around 20%-40%.[46] However, interpretation of this behavior is still being debated.

**C. Comparison.** The segmental relaxation time distributions of PVME/toluene mixtures are about 0.5 decade broader than those of the other mixtures and neat PVME. Although EPh and toluene have similar chemical structures (except the absence of proton-donating species in the latter), the small but noticeable broadening in PVME/toluene cannot be attributed solely to the lack of intermolecular hydrogen bonding. We note that the $T_g$ of toluene is about $-160$ °C,[47] $\sim$93 °C lower than $T_g$ of EPh and $\sim$135 °C lower than that of PVME. Thus, the intrinsic mobility difference between PVME and toluene is quite large. However, the broadening is in fact insignificant when compared with that observed in similar polymer blends, say PS/PVME (also with $\Delta T_g \approx 130$ K), and the difference between PVME/toluene and PVME/PS can be attributed to the enhanced combinatorial entropy contribution to mixing and the absence of chain connectivity in the former mixture. Nevertheless, the slight speeding up of the secondary relaxation of PVME in its mixture with toluene likely results from the absence of intermolecular hydrogen bonding, as compared with the slowdown in mixtures with EPh or BPM.

Although we initially proposed that the two hydroxyl groups in BPM could serve as pseudo-cross-linking agents in the mixture, the increase of $T_g$ in PVME/BPM with increasing BPM concentration cannot be used as direct evidence, since we have not been able to directly measure $T_g$ of neat BPM. The two hydroxyl species per BPM molecule are undoubtedly responsible for its higher melting temperature and crystallizability, compared with those of EPh. The influence of this structure on mixture dynamics can be discerned by comparing the fragility of PVME/BPM with that of PVME/EPh and PVME/toluene mixtures. In mixtures with low small molecule concentrations, the small molecules are randomly distributed in the polymer host, and no clusters should be formed. Recall that the segmental relaxation is a cooperative process, and the cooperativity of PVME segments is a result of both topological constraints and chain connection constraints in neat PVME. However, the cooperativity of one PVME segment cannot be transferred to other segments or small molecules by EPh or toluene in their mixtures as effectively as in neat PVME, since they are unable to associate strongly with other units through hydrogen bonding or chemical bonding. On the other hand, BPM can form a second hydrogen bond with another PVME repeat unit. The cooperativity can be transferred from the first hydrogen-bonded PVME to a second associated PVME unit with BPM acting as the "bridge", in addition to the usual cooperativity through geometrical requirement, although the hydrogen bonding is weak compared with the chemical bond in polymer blends. Fragilities of PVME/BPM mixtures are indeed comparable to that of PVME (Table 1), suggesting that the cooperativity is not "lost", whereas both PVME/EPh and PVME/toluene mixtures exhibit a clear decrease in fragility. This demonstrates the "sticker" effect of BPM. The effect of dual proton-donating groups per molecule can be achieved in mixtures with stronger proton acceptors, e.g., poly(2-vinylpyrridine) [P2VPy]. We found that precipitation occurs immediately when introducing 30% BPM into a P2VPy/MEK solution, suggesting the formation of a relatively extensive network through hydrogen bonding.

In our previous study on the dynamics of PVPh/poly(vinyl ethyl ether) [PVEE] blends, two segmental relaxation processes were resolved in blends with 10% and 20% PVPh.[27] This was rationalized by the stoichiometry of hydrogen bonding. The slow process was attributed to the relaxation of hydrogen-bonded PVPh and PVEE segments and the fast one to unassociated PVEE segments. This behavior, however, cannot be clearly observed in the present case. This can also be explained by considering their significantly different $\Delta T_g$'s and different hydrogen-bonding fractions. First, the very large $\Delta T_g$ (185 K) between PVEE and PVPh indicates significant mobility difference; thus, the hydrogen-bonded and unassociated segments also have very different relaxation times, and their relaxation processes are separated into two discernible peaks. However, the mobility difference between PVME and BPM is relatively small, and the associated and unassociated segments likely have similar relaxation times and, consequently, only a single α process is observed experimentally. Second, as discussed above, the intermolecular hydrogen bond fraction in PVEE/PVPh is considerably lower than that in PVME/BPM at the same composition due to intramolecular screening; thus, the critical concentration for the existence of two kinds of segments in the latter is likely much lower than in the former. This is also why we believe that there is only one kind of relaxing segment in mixtures with BPM or EPh concentrations higher than 10%.

Although we have discussed the damping of CF by the presence of intermolecular hydrogen bonding, this effect becomes clearer when compared with the results of a series of studies on the dynamics of concentrated solutions of PS and PVAc in different solvents.[48] Adachi and co-workers found that solvent quality plays a significant role on the concentration fluctuations. TTS was found to hold in PS/toluene solutions at all concentrations but fails for PVAc/toluene, although the latter has a smaller $\Delta T_g$. Moreover, significant CF were observed in PS solutions in ethylbenzene, *n*-propylbenzene, and *n*-butylbenzene: this was attributed to the deterioration of the solvent quality, compared with toluene. The above results demonstrate that solvent quality, i.e., the effective interaction parameter, is very important in achieving dynamical homogeneity. On the other hand, the importance of $\Delta T_g$ is found in the dielectric relaxation peak broadening observed in mixtures of an azo dye and PMMA, although there is intermolecular hydrogen bonding between the guest and the host.[34] In summary, both intermolecular interactions and $\Delta T_g$ are crucial factors in determining the dynamics in polymer/small molecule mixtures.

## Summary

A broadband dielectric study of mixtures of PVME with three small molecules (EPh, BPM, and toluene) was performed to investigate the influence of chain connectivity and intermolecular hydrogen bonding on segmental dynamics. The first two mixtures exhibit dynamic homogeneity, and TTS was found to be valid. This was interpreted by considering four factors: (1) smaller $\Delta T_g$ compared with the corresponding PVPh/PVME blends, thus smaller mobility differences; (2) damped concentration fluctuations due to intermolecular hydrogen bonding and enhanced mixing entropy; (3) no chain connectivity for the small molecules, thus no self-concentration effect; (4) reduced interchain cooperativity, particularly in mixtures with EPh and toluene. The segmental relaxation time distributions of PVME/toluene mixtures are slightly broadened, resulting from an absence of strong intermolecular hydrogen bonding and a large $\Delta T_g$. The significantly broadened $\alpha$ relaxation time distribution in PVPh/PVME can be attributed to the very large intrinsic mobility difference between the components and chain connectivity.

The $\beta$ relaxation of PVME is broadened considerably at low frequencies for EPh and BPM mixtures, similar to that in PVPh/PVME blends, but is faster in mixtures with toluene. This behavior suggests that intermolecular hydrogen bonding is able to slow down the secondary relaxation. Where spatial heterogeneity is concerned, no unambiguous conclusions can be identified at the present stage, although two kinds of PVME segments, hydrogen-bonded and unassociated, can be resolved by curve fitting the dielectric loss spectrum of the 2% BPM mixture.

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**Supporting Information Available:** Dielectric loss spectra of 2/98, 5/95, and 20/80 BPM/PVME and 10/90 toluene/PVME mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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