Dynamical Heterogeneity in the Thermodynamically Miscible Polymer Blend of Poly(vinyl ethyl ether) and Styrene-*co*-*p*-hydroxystyrene Copolymer

S. H. Zhang, X. Jin, P. C. Painter, and J. Runt*

Department of Materials Science and Engineering and Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

Received April 17, 2003; Revised Manuscript Received June 10, 2003

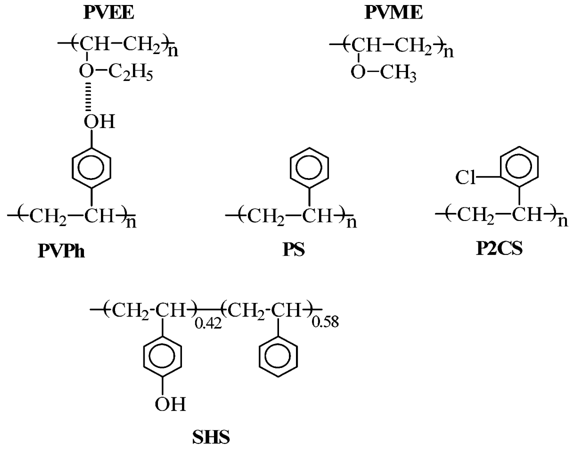
ABSTRACT: The dynamic heterogeneity of the thermodynamically miscible blend of poly(vinyl ethyl ether) and styrene-*co*-*p*-hydroxystyrene (PVEE/SHS) has been investigated using broadband dielectric spectroscopy (DRS) and other experimental probes. In our previous study of PVEE/poly(*p*-hydroxystyrene) blends, we found that the segmental relaxations of the component polymers can be coupled if there is sufficient intermolecular hydrogen bonding. For SHS/PVEE blends, however, two segmental relaxations are observed in the DRS spectra, even for blends with a fraction of intermolecular hydrogen bonds as large as that in the PVPh/PVEE blend, in which a single segmental relaxation was found as a result of the coupling effect from the hydrogen bonds. This behavior is explained by the existence of unfavorable interactions between PVEE and the styrene units in SHS, which is supported by the immiscibility between PS and PVEE. The repulsive force endows the non-hydrogen-bonded PVEE segments with more freedom to relax, so that they can be distinguished from the relaxation of intermolecularly hydrogen-bonded PVEE−SHS segments. This indicates more significant dynamic heterogeneity in SHS/PVEE than in PVEE/poly(*p*-hydroxystyrene) blends.

Introduction

The miscibility of polymer blends is of critical importance for successful material applications, and it is generally believed that only a single calorimetric glass transition temperature (T_g) can be observed if the component polymers are thermodynamically miscible. The T_g in differential scanning calorimetry (DSC) experiments is usually defined as the midpoint of the heat capacity (ΔC_p) jump, which is a result of gaining mobility to adapt different conformations due to the increase in fractional free volume and enhanced thermal activation energy.[1] Since the calorimetric T_g represents an increase of chain mobility, a single T_g in a thermodynamically miscible polymer blend immediately suggests that the components have the same mobility at the T_g of the blend, and a single dielectric (DRS) or dynamic mechanical (DMA) segmental relaxation process is expected in such systems. The correlation between a single calorimetric T_g and a single dynamic segmental relaxation process in miscible polymer blends has been confirmed by studies on different systems.[2,3]

Nevertheless, recent studies have shown that dynamic heterogeneity dominates the relaxation behavior of miscible polymer blends having large T_g difference (ΔT_g) and weak intermolecular interactions. Two separated segmental relaxation processes, corresponding to the individual components, are sometimes observed, representing extreme heterogeneity. Most of these studies have been performed on blends of polyisoprene with poly(vinyl ethylene) (PIP/PVE),[4−12] polystyrene with poly(vinyl methyl ether) (PS/PVME),[13−20] and poly(2-chlorostyrene) with PVME (P2CS/PVME),[21] using multidimensional nuclear magnetic resonance (NMR), DMA, or broadband dielectric spectroscopy (DRS). The dynamic heterogeneity in these blends has been attributed to either concentration fluctuations (CF),[22−24] component intrinsic mobility differences, or chain connectivity effects.[25−27]

Scheme 1. Chemical Structures of Model Polymers



We have recently studied the dynamic relaxations of the miscible blend of poly(*p*-hydroxystyrene) [= poly(4-vinylphenol) (PVPh)] with poly(vinyl ethyl ether) (PVEE).[28] Segments of these two polymers might at first be expected to relax individually, since they have chemical structures similar to PS/PVME and P2CS/PVME blends and even larger ΔT_g (Scheme 1 and Table 1). Nevertheless, for PVPh/PVEE blends with PVPh concentration ≥ 30%, a single segmental relaxation process was observed in our broadband dielectric study. This was attributed to the ability of the strong intermolecular hydrogen bonds between PVPh and PVEE to couple the component segmental relaxations, even though their mobilities are very different ($\Delta T_g \sim 186$ K). For blends with lower PVPh content, however, two dielectric segmental relaxation processes were observed.

---

* To whom correspondence should be addressed: e-mail runt@matse.psu.edu; phone 1-814-8632749; fax 1-814-8652917.

10.1021/ma034501r CCC: $25.00

Table 1. Comparison of ΔT_g and Interaction Parameters in Selected Polymer Blends

	PIP/PVE	PS/PVME	P2CS/PVME	SHS/PVEE	PVPh/PVEE
ΔT_g (K)	59	130	154	172	185
χ^a	~ -0.002	~ -0.01		< -1.0	< -1.0
intermolecular interactions	van der Waals	van der Waals	dipole−dipole	hydrogen bonding	hydrogen bonding
reference	30	19	21	38	28, 38

[a] Dependent on composition and temperature. The values shown represent the typical magnitude of the reported interaction strength.

This is due to a *stoichiometric* effect: the slow dielectric segmental process was attributed to the relaxation of intermolecularly hydrogen-bonded PVPh and PVEE segments and the fast one to non-hydrogen-bonded ("free") PVEE segments. At these compositions, the overall hydroxyl group concentration is low, and a portion of the PVEE segments are free from hydrogen bonding. For [PVPh] ≥ 30%, almost all PVEE segments are hydrogen bonded with PVPh and the fast process disappears. We also observed similar behavior in blends of PVPh with an ethylene/vinyl acetate random copolymer (vinyl acetate content of 70%, EVA70).[29]

These findings also suggest that intermolecular interactions play a more important role in establishing the dynamic heterogeneity than ΔT_g. For example (Table 1), although ΔT_g is as small as 59 K for the PIP/PVE blend, the marginally negative interaction parameter ($\chi \sim -0.002^{30}$) still leads to significant dynamic heterogeneity, whereas although the interaction is only slightly stronger in PS/PVME ($\chi \sim -0.01^{19}$), a very large ΔT_g ($\sim$130 K) is needed to retain similar heterogeneity. By introducing much stronger hydrogen bonds, this dynamic inhomogeneity can be completely eliminated in PVPh/PVEE blends with certain compositions.

In the present paper, we report our new DRS results on blends of PVEE with a random copolymer of styrene and *p*-hydroxystyrene (SHS). The dynamic properties of SHS/PVEE are expected to combine the heterogeneity observed in PS/PVME and the homogeneity in PVPh/PVEE blends. Furthermore, the hydrogen bond strength between the phenolic −OH and ether oxygen should be approximately the same as that between similar functionality in PVEE and PVPh, but the intermolecular hydrogen bond fraction is lower in the former at the same blend composition by weight due to dilution by the styrene units. Comparison of the segmental relaxation behavior of the two blends tests the validity of the stoichiometric model proposed previously for PVPh/PVEE blends. In addition, the influence of the nonpolar styrene units on the dynamic heterogeneity will be discussed.

Experimental Section

A. Materials and Sample Preparation. PVEE was purchased from Monomer−Polymer & DAJAC Laboratories, Inc., and has $M_w = 27\,000$ and $M_w/M_n = 2.1$. It was used without further purification. SHS was obtained from Hoechst Celanese and fractionated using a multiple precipitation procedure, employing an acetone/water mixture. The fraction with $M_w = 28\,000$ and $M_w/M_n = 2.6$ was used in this study. The *p*-hydroxystyrene comonomer composition in this copolymer was determined to be 42 mol % by ^{1}H NMR. Molecular weights of both polymers were determined by gel permeation chromatography using dimethylformamide as the mobile phase and narrow molecular weight distribution poly(ethylene oxide) standards.

Blends with SHS concentrations from 20 to 70 wt % were prepared by solution casting. Initially, 5 wt % solutions of the neat polymers in methyl ethyl ketone were prepared, and then the appropriate amounts of each were mixed to provide the desired blend composition. The mixed solutions were stirred for at least 30 min before being cast into Teflon-coated foil dishes. The solvent was removed in a vacuum oven by gradually increasing the temperature ($\sim$5 K/12 h heating rate) up to $T_g + 20$ K. All films were $\sim$100 μm in thickness. For DRS studies, gold was sputtered on both sides of the samples in an argon atmosphere for samples with T_g above room temperature. For PVEE and the 20% blend, whose T_g's are well below ambient temperature, gold sputtering was not attempted; these samples were sandwiched between two electrodes, and a polypropylene spacer was used to control the thickness.

Samples for DSC were prepared by slowly dropping the mixed solutions into individual aluminum DSC pans and then following the same thermal procedure as in the DRS study.

B. DRS Experiments. Dielectric spectra $\epsilon^*(f,T)$ were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency domain (0.01 Hz−4 MHz) on cooling from $T_g + 60$ K to T_g. Sample films were held between two parallel gold-sputtered steel electrodes, having a diameter of 20 mm. 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.

C. DSC. DSC experiments were performed using a Seiko SSC 5200 DSC with sample weight $\sim$10 mg. The instrument was calibrated with three standards: tin, indium, and cyclohexane. The samples were first heated to 50 K above the expected T_g, held for 3 min, and then cooled at a rate of 20 K/min. After soaking at a minimum temperature ($T_g - 40$ K) 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. Nitrogen was used to purge the sample chamber at a rate of 60 mL/min for blends with SHS concentration ≥ 40%.

D. FTIR. FTIR spectra were recorded on a Bio-Rad FTS-6 spectrometer with a resolution of 2 cm^{-1} by averaging 64 scans. Sample solutions were coated onto KBr windows, and the solvent was removed in a heated vacuum oven.

Results

A. Miscibility between SHS and PVEE. There have been extensive studies of the miscibility of polymer blends with intermolecular hydrogen bonds.[31] Generally, miscibility can be achieved between otherwise immiscible polymer pairs if sufficient intermolecular hydrogen bonding can be induced in order to balance the unfavorable repulsive interactions between the components. Although the fraction of intermolecular hydrogen bonding in SHS/PVEE blends is lower than the corresponding blend of PVPh and PVEE at the same weight composition, the former blend is nevertheless miscible, as confirmed by our DSC results, in which a single T_g was observed for each blend used in the DRS study (Figure 1). The glass transition in of the blends is relatively broad (from 21 to 32 K), compared to the $\sim$10 K breadth for the T_g interval of neat SHS and PVEE. However, this broadness is less than that of similar PVME/P2CS blends ($\sim$25−60 K).[21] The broadening of the glass transition in miscible polymer blends has been interpreted by invoking either chain connectivity effects or concentration fluctuations.

B. Hydrogen Bonding in the Blends. FTIR has been widely used to measure the inter- and intramo-

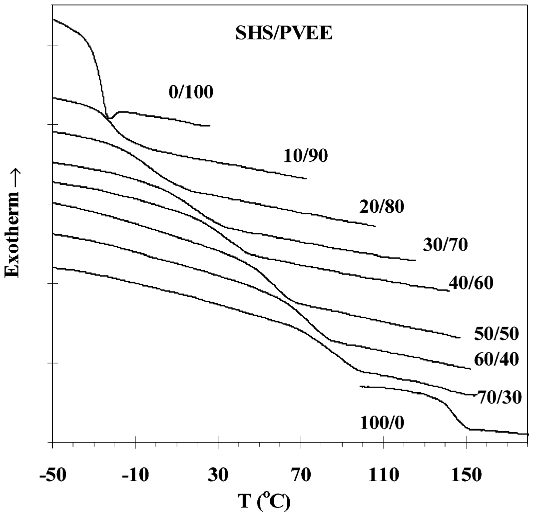


Figure 1. DSC curves of SHS/PVEE blends: second heating run, heating rate = 10 K/min.

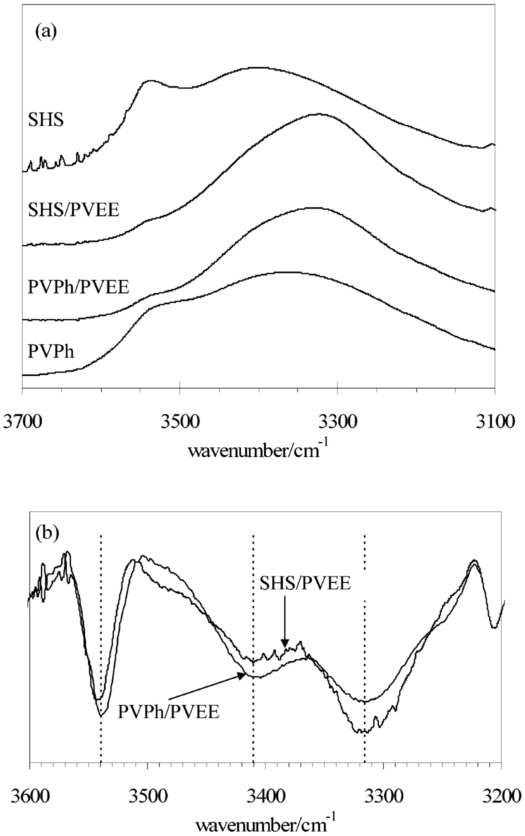


Figure 2. (a) FTIR spectra of PVPh, SHS, and their 50% blends with PVEE at room temperature. (b) Second-derivative spectra of 50% SHS/PVEE and PVPh/PVEE blends at room temperature.

lecular hydrogen-bonding degree and strength in polymer blends. Figure 2 presents the IR spectra of neat PVPh, SHS, and their blends with PVEE. The broad peak above 3000 cm^{-1} includes contributions from the stretching modes of free, intramolecularly bonded, and intermolecularly bonded −OH groups, from high to low cm^{-1}. The band at ~3315 cm^{-1} arises from intermolecularly hydrogen-bonded hydroxyl groups, and its high absorbance indicates the existence of a large fraction of hydroxyl−ether bonding. The frequency shift of this band from that of the free OH stretching mode is a measure of the hydrogen bond strength. Larger shifts ($\Delta\nu$) indicate stronger interactions. Since there are several bands close to each other in this spectral region, it is difficult to determine their precise location. To resolve this, the second derivative of each spectrum was calculated (Figure 2b), in which the original band becomes much narrower and the minimum provides its location. It is clearly seen that the intermolecular hydrogen bond, with a $\Delta\nu$ of 225 cm^{-1}, is much stronger than the intramolecular one ($\Delta\nu \sim 95$ cm^{-1}). Since PVPh and SHS have the same proton-donating group and similar chain structure, their intermolecular hydrogen bonds with PVEE ether groups have the same strength, as confirmed in the second-derivative spectra.

C. Dielectric Relaxation of PVEE and SHS. The dielectric relaxation behavior of PVEE was reported in our recent paper.[28] Two relaxation processes, α and β, were observed. The α process in PVEE occurs above T_g, and its dependence on temperature is non-Arrhenius, characteristic of a cooperative relaxation process. As observed in other homopolymers, the segmental relaxation time distribution of PVEE is broader than a single Debye process but relatively narrow compared to that observed in the blends.

The α relaxation of neat SHS is well-defined only at temperatures ~20 K above its T_g. Close to T_g, it is masked by strong dc conduction at lower frequency. Below 40 °C, a local relaxation process moves into the frequency window and shifts to low frequency with decreasing temperature. Since its intensity is weak ($\epsilon_{\max}'' < 10^{-2}$), we will not consider it when analyzing the segmental relaxations in the blends.

D. Segmental Relaxation of the Blends. Although the dipole moment of styrene is close to 0, *p*-ethylphenol, a model compound for *p*-hydroxystyrene, has a dipole moment of ~1.61 D in benzene. This leads to a monomer-averaged effective dipole moment of about 0.68 D for an SHS copolymer with 42 mol % *p*-hydroxystyrene. Ethyl ethyl ether, a model for the repeat unit of PVEE, has a dipole moment of 1.25 D in benzene.[32] Since both polymers are dielectrically active, the observed dielectric segmental relaxation in blends includes contributions from both PVEE and SHS.

As an example, Figure 3 shows the dielectric loss (ϵ'') spectra of blends with SHS concentrations of 20%, 30%, and 40% at selected temperatures above the corresponding T_g. The 20% blend exhibits clear low-frequency broadening, and the spectra become narrower with increasing temperature. Conversely, a high-frequency shoulder is observed in the 40% blend. This shoulder is visible even at temperatures far above T_g, and its intensity is much stronger than that of the local relaxation process observed in neat SHS, excluding this as its origin. The α relaxation of the 30% blend exhibits a relatively symmetric relaxation peak. Blends with SHS concentration of 50%, 60%, and 70% have the same relaxation behavior as that observed for the 40% blend. The evolution from a low- to high-frequency shoulder is more clearly demonstrated by directly comparing the dielectric spectra of the different blends at normalized temperatures (Figure 4). When the primary relaxation is located between approximately 1−10 Hz (at a low temperature close to the corresponding T_g, Figure 4a), blends with SHS concentration ≥40% exhibit very clear high-frequency shoulders, whereas at ~100−1000 Hz (at a higher temperature, relatively far above T_g, Figure 4b), the high-frequency shoulder in the 40% blend

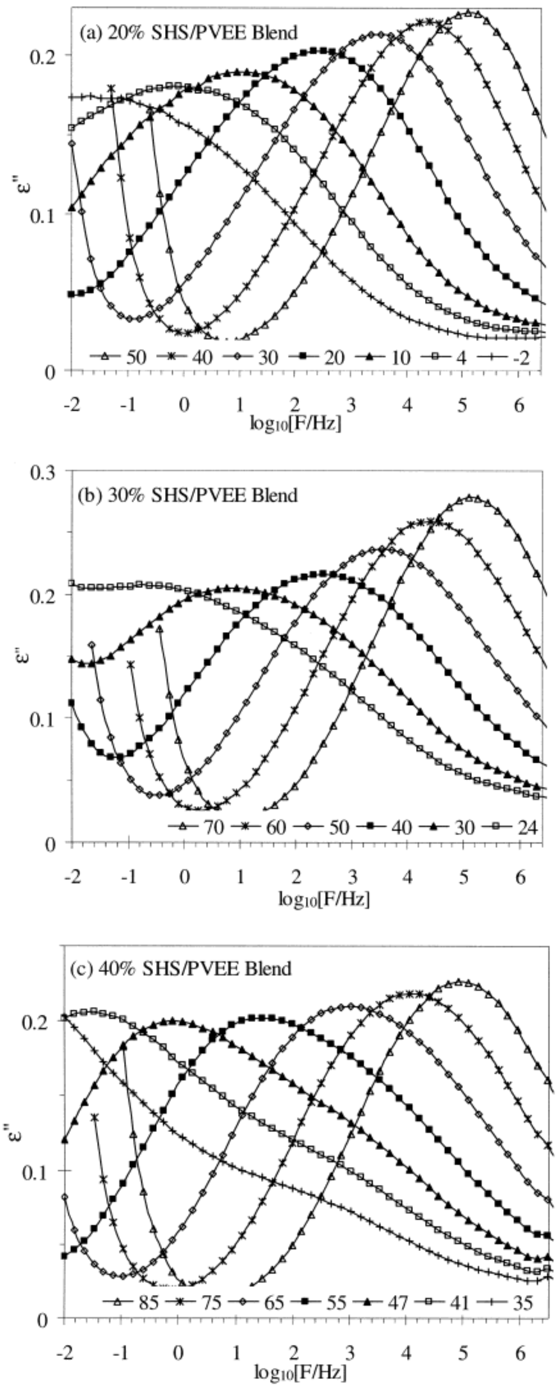


Figure 3. DRS loss spectra of SHS/PVEE blends with SHS concentration of (a) 20%, (b) 30%, and (c) 40%. The labels in each figure give corresponding temperatures in °C. For clarity, only spectra at selected temperatures are presented.

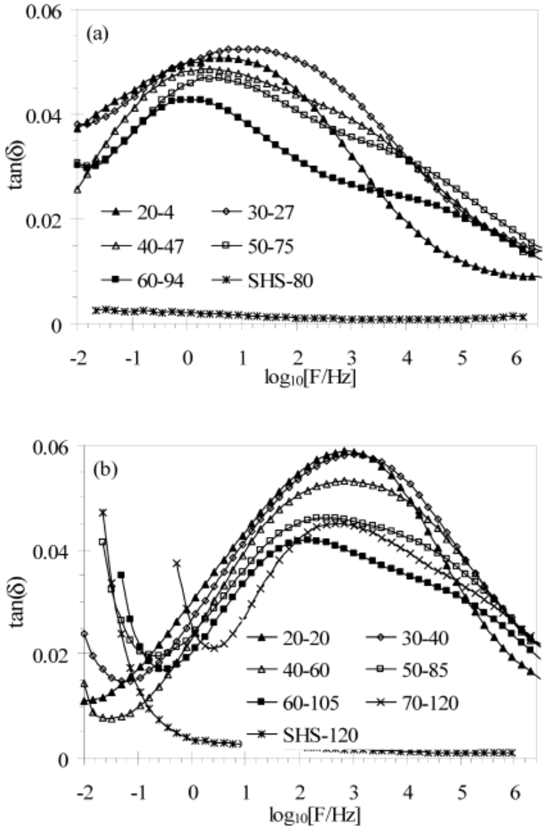


Figure 4. Comparison of the segmental relaxations of SHS/PVEE blends with different compositions with peak locations at (a) ~2 Hz and (b) ~1 kHz. The first number in the label is the concentration of SHS (in wt %), and the second number represents the corresponding temperature in °C.

merges with the slow relaxation process and is difficult to define. The increase in the relaxation rate is faster for the slow, than the fast, process due to the higher activation energy of the former, and merging of the processes is a natural consequence. For blends with higher SHS concentrations, however, the fast process can still be clearly observed, suggesting a larger difference between the fast and slow processes in these blends. Again, the β relaxation of SHS at a similar temperature is very weak and does not contribute to the strong fast process, as shown in Figure 4. As will be discussed later, we attribute the high-frequency shoulder to the relaxation of non-hydrogen-bonded PVEE segments, similar to the assignment in PVPh/PVEE blends.

It is well-known that the segmental relaxation time distribution in polymers is generally quite broad and asymmetric. It is often fitted with the phenomenological Havriliak−Negami (HN) equation, which introduces two shape parameters, m and n, to describe the breadth and asymmetry:[33,34]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty - i\frac{\sigma_0}{(\epsilon_v\omega)^s} + \frac{\Delta\epsilon}{[1 + (i\tau_{HN}\omega)^m]^n} \quad (1)$$

in which $\omega = 2\pi f$, ϵ_∞ and ϵ_R are the unrelaxed and relaxed dielectric constant (ϵ') at very high and low frequency, respectively, and $\Delta\epsilon = \epsilon_\infty - \epsilon_R$ is the relaxation strength. ϵ_v is the vacuum permittivity, and σ_0 is the dc conduction constant with units of S/cm; the exponent s ($0 < s \leq 1$, s found to be ~1) characterizes the conduction process. σ_0, s, τ_{HN}, $\Delta\epsilon$, m, and n are free variables in fitting the DRS loss spectra, ϵ''. The relaxation time τ_{max}, defined as the location of the peak maximum, can be calculated from τ_{HN} with eq 2:[3]

$$\tau_{max} = \tau_{HN}\left[\frac{\sin\frac{\pi m n}{2(n+1)}}{\sin\frac{\pi m}{2(n+1)}}\right]^{1/m} \quad (2)$$

From the previous discussion, it is clear that the segmental relaxation distributions in SHS/PVEE blends

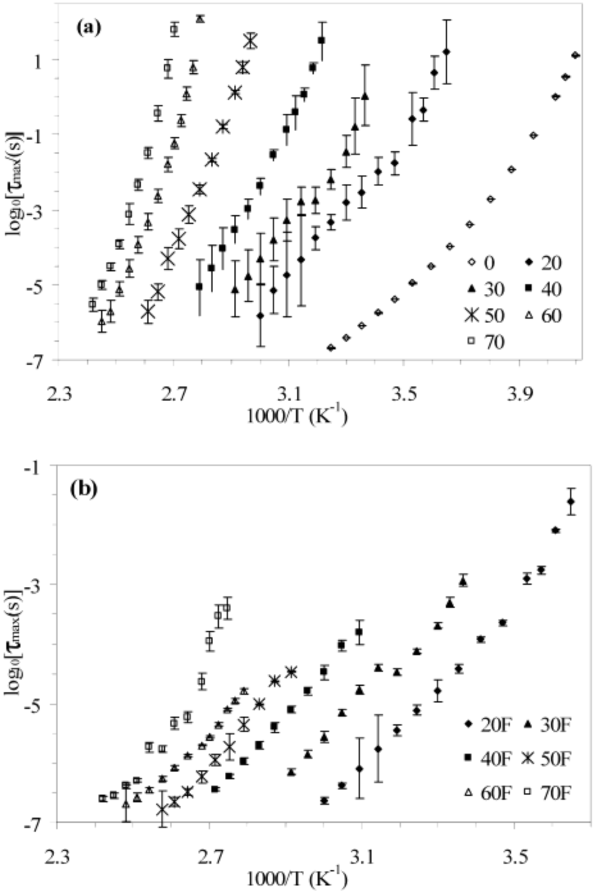


Figure 5. Arrhenius plots of SHS/PVEE blends: (a) slow and (b) fast process. The number in the label indicates the weight concentration of SHS in %.

cannot be fitted with one relaxation process. This supports the argument that there are at least two types of relaxing segments in the blend. However, these processes are very close to each other in the 20% and 30% blends at all temperatures and in other blends at higher temperatures. Fitting the DRS spectrum with two relaxation processes, i.e., with more than eight free variables, leads to an unstable regression, and completely different sets of parameters can give similar overall fits. For these spectra, we fixed the shape parameter $n = 1$ for the fast process, which reduces the HN equation to the Cole−Cole function, and extrapolation from fitting results below T_g (in which only the fast process can be observed) was used to guide the fitting. The fitting gives physically reasonable results compared with those for blends containing 40%−70% SHS at temperatures where the two processes are sufficiently separated and well-defined (Figure 5). It is clear from Figure 5 that the low-frequency relaxation becomes significantly slower with increasing SHS content as a result of increased T_g. The fast relaxation process exhibits similar slowdown behavior, but this is less significant than that for the slower process. The slow and fast processes in blends with 30% and 40% SHS are close to one another, and the uncertainty in their relaxation time is quite large (Figure 5a). On the other hand, they are well separated and can be defined with more confidence in blends with 50−70% SHS content.

Discussion

The influence of hydrogen bonding on polymer dynamical properties has been studied by several groups using different experimental methods. First, as mentioned above, in our dielectric study on PVPh/PVEE we found that intermolecular hydrogen bonds are capable of coupling the segmental relaxations of PVPh and PVEE.[28] A single α process was observed when all PVEE segments are hydrogen-bonded with PVPh. It may be questioned that a single peak in the latter blends does not necessarily imply a single segmental process, but a fast process may be located in the high-frequency tail of the slow one and simply cannot be observed. This is not correct on the basis of the successful application of the time−temperature superposition (TTS) principle for blends with [PVPh] ≥ 30% but failure for the 10% and 20% blends. Nonassociated PVEE repeat units do exist; however, their relaxations have been coupled with these of PVPh and associated PVEE through nearby hydrogen bonding, although not necessarily with exactly the same rate. Similar behavior has also been observed in a recent CPMAS ^{13}C NMR study of poly(vinyl acetate)/poly(methacrylic acid) [PVAc/PMAA] blends.[35] It was found that these blends are miscible at the 2−5 nm length scale for PMAA-rich (proton donor) blends, whereas for PVAc-rich blends they are heterogeneous at this length scale and only homogeneous at a larger 20−50 nm scale. The authors concluded that 30% of the possible hydrogen-bonding interactions are needed to obtain miscibility at the segmental scale. The 2−5 nm length scale is close to the size of the cooperatively rearranging size (CRR) near T_g, which is generally believed to be the scale for segmental relaxation, and decreases rapidly with increasing temperature. These CPMAS ^{13}C NMR results support the stoichiometric model. That is, for PVAc-rich blends, a portion of the PVAc segments are not hydrogen-bonded with PMAA, and heterogeneity at the 2−5 nm scale is a natural consequence.

The effect of interaction stoichiometry has also been observed in FTIR orientation-relaxation studies on PVPh/PVME[36] and PVPh/poly(ethylene oxide) [PEO][37] blends. Brisson and co-workers concluded that intermolecular hydrogen bonds hinder segmental relaxation, and the orientation reaches a maximum when the molar ratio of functional groups involved in the intermolecular hydrogen bonding reaches 1:1.

It is important to point out that one segment, i.e., the unit relaxing in the DRS experiment, consists of several to several tens of repeat units, depending on the temperature. It is not necessary to bond every pair of proton donor−acceptor groups to couple their orientation or relaxations to provide homogeneity (a single α process) at the segmental scale. Considering that there is also significant intramolecular hydrogen bonding in the proton donor polymers (i.e., PVPh, SHS, or PMAA), a 1:1 molar ratio between the two interacting groups in the blend does not necessarily lead to maximum intermolecular interactions and finer dynamic homogeneity, although more intermolecular interactions undoubtedly favor greater miscibility/homogeneity.

However, the results for the SHS/PVEE blends presented above do not appear at first to be consistent with expectations from the stoichiometric model, although the components have similar chemical structures and hydrogen bond strengths compared to PVPh/PVEE. To reiterate, we found that for a 30 wt % PVPh/PVEE blend, with a molar ratio of −OH/−O− of about 1:3.9 and an intermolecular hydrogen-bonding fraction of 22% (per −O−, at 50 °C), is sufficient to couple all PVEE segments, and thus the fast relaxation from "free" PVEE

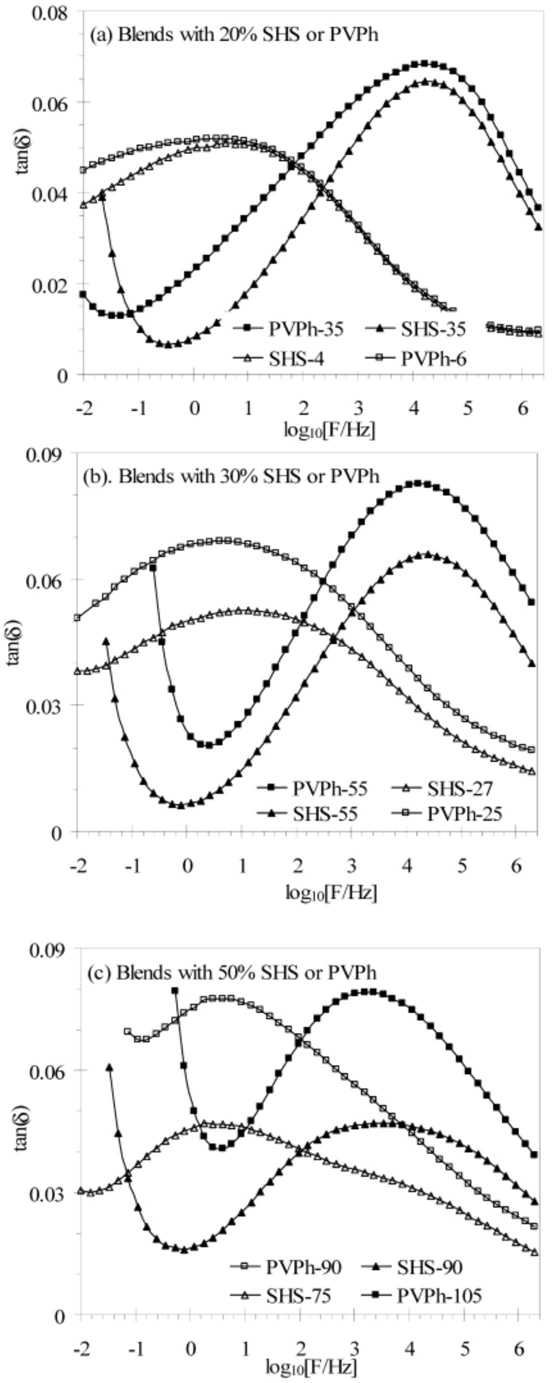


Figure 6. Comparison of isothermal dielectric spectra of SHS/PVEE and PVPh/PVEE blends with SHS or PVPh concentration of (a) 20%, (b) 30%, and (c) 50%.

segments disappears.[28] The same functional group ratio can be achieved in SHS/PVEE blends with an SHS content of ∼50 wt %. That is, above this ratio, since all PVEE segments are expected to be hydrogen-bonded with SHS, the SHS/PVEE blend should exhibit a single segmental relaxation process. This is provided of course that intermolecular hydrogen bonding is the dominant factor influencing the dynamics.

A detailed comparison of DRS spectra of SHS/PVEE with those of PVPh/PVEE provides additional insight into the origin of the dynamic heterogeneity in the SHS/PVEE blend system. For blends with 20% PVPh or SHS, similar low-frequency broadening is observed (Figure 6a). Because the intermolecular hydrogen bond fraction for PVEE is higher with PVPh than SHS, more PVEE segments are involved in the slow relaxation process in PVEE/PVPh blends. This is supported by the stronger low-frequency shoulder in the PVPh/PVEE blend, compared to SHS/PVEE, at similar normalized temperatures.

For 30% PVPh and SHS blends, the segmental processes become more or less symmetric for both (Figure 6b). This is reasonable since the degree of intermolecular hydrogen bonding has increased compared with the 20% blend. However, the single dielectric peak does not necessarily mean that there is a single relaxing unit for the 30% SHS/PVEE blend. It is possible that two types of segments are relaxing with rates close to one another (i.e., separated by less than ∼2−3 decades) and thus appear as one broad peak. We propose that only one relaxing segment is present in the 30% PVPh/PVEE blend, but two in the comparable SHS/PVEE blend. This is supported by examining the DRS spectra of the 50% blends (Figure 6c), in which the PVPh/PVEE blend still exhibits one segmental relaxation process, but two processes become more evident in SHS/PVEE. We have also found that time−temperature superposition principle (TTS) can be applied to the 50% PVPh/PVEE blend,[28] but it clearly fails for the comparable SHS blend. Two segmental relaxation processes are also been observed in 60% and 70% SHS/PVEE blends.

Since the hydrogen-bonded fraction of PVEE increases with increasing PVPh, one may attempt to attribute the fast relaxation process in blends with high PVPh concentration to the relaxation of PVEE segments with weaker, but still hydrogen-bonded with PVPh, coupling degree. This is not true considering that the distribution of the coupling degree should be smooth, and thus no visible shoulder can be expected.

The apparent contradictory results between chemically similar SHS/PVEE and PVPh/PVEE blends lead to a natural question: is the intermolecular hydrogen bond fraction in the former sufficiently high to couple the segmental relaxations? Recall that the two segments have the same hydrogen bond strength (Figure 2). Since the FTIR peaks of free −OH and intra- and intermolecularly bonded −OH are close to one other, curve fitting is unreliable, and it is difficult to determine the hydrogen bond fractions between ether and hydroxyl groups. However, on the basis of previous studies, this fraction can be theoretically calculated if the equilibrium constant for hydrogen bonding is known.[31] Using the intermolecular hydrogen-bonding strength and equilibrium constants determined from model compounds, and assuming the same hydrogen-bonding energy for SHS and PVPh (listed in Table 2, together with other parameters used in the calculations), we are able to calculate intermolecular hydrogen bond fractions (Figure 7). At 100 °C it is estimated that ∼18% of the PVEE ether groups are associated with hydroxyl groups in the 30% PVPh/PVEE blend; the same fraction is achieved in a ∼50% SHS/PVEE blend. In other words, at 50 °C, 53% SHS is required to produce the same coupling effect as in a 30% PVPh blend. Therefore, the unexpected dynamic heterogeneity in 50−70% SHS/PVEE blends is *not* a result of an insufficient number of intermolecular hydrogen bonds. Consequently, the relaxation behavior should be interpreted by considering the primary difference between PVPh and SHS, that is, the presence of the styrene comonomer units.

Table 2. Parameters Used To Calculate Intermolecular Hydrogen Bond Fractions[a]

	molar volume (cm^3/mol)	solubility parameter (cal cm^{-3})$^{-0.5}$	equilibrium constants of hydrogen bond formation at 25 °C[b]		
			K_2	K_B	K_A
PVPh	100	10.6	21.0	66.8	88.3
SHS	224.5	10.0	9.4	29.8	39.3
PVEE	71.8	8.4			

[a] These parameters were taken from ref 31, and the intramolecular screening factor was set to be 0.3 for both blends. [b] K_2: for intramolecular dimer formation; K_B: for intramolecular multimer formation; K_A: for intermolecular hydrogen bond between PVEE and PVPh or SHS. Corresponding enthalpy of hydrogen bond formation: $h_2 = -5.60$, $h_B = -5.20$, and $h_A = -5.4$ kcal/mol.

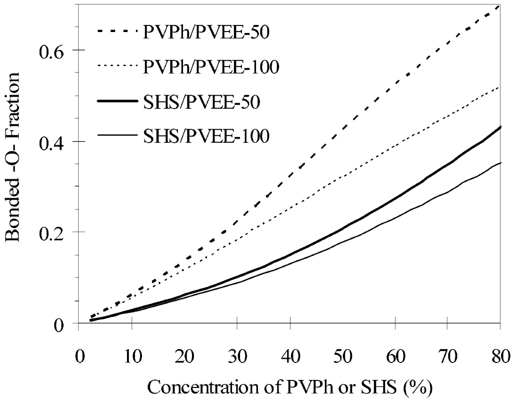


Figure 7. Calculated hydrogen bond fraction in SHS/PVEE and PVPh/PVEE blends at 100 and 50 °C.

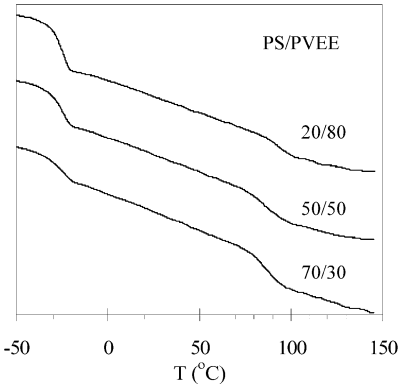


Figure 8. DSC curves of PS/PVEE blends: heating rate = 10 K/min.

It is well-known that PS and PVME are miscible across the composition window, and the miscibility is attributed to the interaction between the aromatic ring in PS and the PVME ether oxygen.[13-20] An analogous weak interaction should also exist between styrene and PVEE. However, simple DSC experiments show two T_g's in PS/PVEE blends with 20%, 50%, and 70% PS (Figure 8, M_w of PS ~ 100 000), very close to the corresponding T_g's of neat PVEE and PS. This immediately demonstrates that PS and PVEE are immiscible and that the interaction between PS and PVEE is unfavorable (i.e., a positive χ). This is sensible considering the relatively larger size of the ethyl group in PVEE, compared with $-CH_3$ in PVME, which acts to shield the ether oxygen atoms from interacting with the aromatic rings.

The situation for the SHS/PVEE blends is therefore more complex than for the corresponding PVPh/PVEE blends: in addition to the strong intermolecular hydrogen bonding between *p*-hydroxystyrene units and PVEE, we must consider the repulsive interaction between styrene units and PVEE. The former are very strong, having an effective $\chi < -1$, and thermodynamic miscibility can be achieved.[38] However, the latter influences the blend dynamics at the very local level.

The relaxation behavior of the SHS/PVEE blends can be explained in a fashion similar to that in PVPh/PVEE: the slower process arises from intermolecularly hydrogen-bonded PVEE-SHS segments, while the fast one arises from nonassociated PVEE segments. The only, but important, difference lies in the manner in which the free PVEE segments relax. In blends with PVPh, the unassociated PVEE segments are strongly geometrically constrained by the large number of neighboring hydrogen-bonded units. Therefore, the dynamical difference between "unassociated" and hydrogen-bonded PVEE segments can be relatively small, and a single α relaxation process is possible. On the other hand, the repulsive interaction between styrene and PVEE units alleviates constraints from the hydrogen-bonded neighborhood upon unassociated PVEE segments. Therefore, the repulsive forces lead to the faster relaxation of unassociated PVEE segments in SHS blends than in PVPh blends. This further suggests a greater difference in the relaxation rate between free PVEE and hydrogen-bonded PVEE−SHS than the corresponding difference in PVEE/PVPh, that is, more significant dynamic heterogeneity in the former blend than in the latter. For blends with SHS concentration < 50%, the dynamic heterogeneity can be interpreted by the stoichiometric model and the repulsion between styrene and PVEE repeat units, whereas for those with [SHS] ≥ 50%, the repulsion plays a more important role.

The relatively weak dipole moment of SHS is also responsible for the *observation* of dynamical heterogeneity in SHS/PVEE blends since it decreases the dielectric relaxation strength of the slow process. Forming intermolecular hydrogen bonds in polymer blends requires corresponding functional groups at appropriate distances and in appropriate directions. Intramolecular screening reduces the equilibrium constant and exaggerates heterogeneity.[38-40] Whereas some segments are coupled with more than the average number of intermolecular hydrogen bonds, unassociated PVEE segments likely exist even at high SHS or PVPh concentrations (>50%). In PVPh/PVEE, because of the strong dipole moment of PVPh, higher intermolecular hydrogen bond fraction, and smaller dynamic heterogeneity, the relaxation of any free PVEE segments would be expected to be very weak and close to the slow process, and thus it is completely masked. However, the reduced strength of the slow relaxation process in SHS/PVEE blends, resulting from the smaller effective dipole moment of SHS, allows the relaxation of unassociated PVEE segments to become more visible; the former does not mask the latter as occurs in PVPh/PVEE, in which the hydrogen-bonded PVPh−PVEE segments dominate the spectra. Therefore, we propose that the unfavorable interactions and dilution from the styrene repeat units are responsible for the observed dynamic heterogeneity in SHS/PVEE.

Recently, chain connectivity effects have been successfully used to explain the dynamic heterogeneity in several polymer blends.[25-27] The main point is that each component experiences a local environment rich in itself compared with the bulk concentration due to chain connectivity, which consequently leads to the dynamical heterogeneity in polymer blends. The chain connectivity model cannot be directly used to interpret the dynamic heterogeneity in SHS/PVEE, since one of its main assumptions is the absence of specific interactions between components, which will bias the local packing.[25]

The dynamic heterogeneity is a natural consequence of the interplay between the favorable intermolecular hydrogen bonding and the repulsive interactions between styrene and PVEE. At the segmental scale, miscibility implies close proximity of the component polymers (i.e., interpenetrating), which contributes to the negative blending enthalpy. Since segmental relaxation is a cooperative process and consists of the movement of many repeat units, this suggests that the two components should relax cooperatively with similar rates. However, in PS/PVME or P2CS/PVME,[21] because of the large intrinsic mobility difference, the thermal energy at temperatures slightly above the global T_g are not sufficient for the high-T_g polymer (i.e., PS or P2CS) to move, and its chains are rigid. Therefore, the low-T_g PVME relaxes within a rigid environment with limited freedom, which explains why its relaxation is slower than in neat PVME. The high-T_g component can only gain mobility at higher temperature, which is lower than its intrinsic T_g, since contact with PVME has alleviated its intramolecular confinement. The weak van der Waals interaction manifests itself by changing the intermolecular fricative coefficient and reducing the mobility difference, but it is not sufficiently strong to link different segments and they can still relax individually. The widely observed dynamic heterogeneity can be a direct consequence of the intrinsic mobility difference.

For blends with strong intermolecular interactions, the cooperativity between two components becomes so significant that they can possibly relax with very close rates or even simultaneously. We have found that the fragility of hydrogen-bonded blends is higher than the neat low-T_g component in PVAc, EVA70, and PVEE blends with PVPh,[28,29] indicating a stronger degree of cooperativity of the segmental relaxations, based on the correlation between cooperativity and fragility.[41−43] At the molecular scale, this can be explained by considering the enhanced friction coefficient between PVEE and the proton-donor polymers as a result of hydrogen bonding. The strong frication force retards the relaxation of the former and accelerates the later. This reduces the components' mobility difference in the blend, and significant coupling of relaxations is a natural consequence.

Formation of a hydrogen bond is only possible when two functional groups (−OH and −O−) are positioned in specific directions and distances (∼0.2 nm). This suggests homogeneity at a smaller scale than in blends without strong intermolecular interactions, in which the distance between two dissimilar chains may be larger. However, this does not necessarily mean that the intermolecular hydrogen bond remains closed during the relaxation of the two parent segments that it links because this requires the −OH and its partner −O− to remain at same relative orientations and distance. Hydrogen bonding is of course dynamic, and there is an equilibrium between breaking and re-forming. During the relaxation of parent segments, one hydrogen bond may break for a short time, but forming a new linkage with another functional group far away would generally be difficult due to the strict geometric requirements and the availability of free functional groups. This broken hydrogen bond is highly likely to re-form between the original two partners until another appropriate functional group is available, which is realized by the relaxation the segments. The second candidate for a hydrogen-bonding partner is the functional groups neighboring to the original one, likely within the same relaxation segment. This leads to an effective, prolonged lifetime for the hydrogen bond. The same mechanism has been invoked in a model for reversible transient networks by Rubinstein and Semenov.[44]

Finally, the effect of intermolecular hydrogen bonds on the dynamic (and static) heterogeneity is more complicated than described by our earlier static stoichiometric model. As pointed out recently, in polymer blends without strong intermolecular interactions, different chains can distribute randomly without significant preference,[25] when the thermal energy is larger than or comparable to the magnitude of intermolecular van der Waals force. However, in SHS/PVEE, the two components strongly prefer to be immediate neighbors to each other in order to form intermolecular hydrogen bonds; thermal concentration fluctuations are retarded, and the heterogeneity is mainly determined by the stoichiometric effect. If the intermolecular hydrogen bonding is very strong, the blends can be macroscopically separated into a 1:1 polymer complex and a neat polymer phase.[45] For even stronger intermolecular interactions, e.g., ionic interactions, ionic clusters are formed. In other words, the hydrogen bonding leads to the heterogeneity in polymer blends. Therefore, hydrogen bonding usually enhances the heterogeneity unless the components are in appropriate ratios.

Summary

Dynamic heterogeneity has been observed in thermodynamically miscible SHS/PVEE blends. Whereas this is reasonable for blends with low SHS content due to the coexistence of hydrogen-bonded and nonassociated PVEE segments, it was quite unexpected for high SHS content blends. The presence of a high-frequency shoulder in the latter suggests that unassociated PVEE segments still exist. The interaction between the styrene comonomer units in SHS and PVEE repeat units is unfavorable, and we propose that this repulsive force relieves the constraint experienced by free PVEE segments. This leads to more significant dynamic heterogeneity than observed in PVPh/PVEE blends, and the fast relaxation becomes more visible as a result of the weakened slow process due to dilution by nonpolar styrene in SHS. Finally, evidence acquired thus far supports the idea that intermolecular hydrogen bonding effectively freezes the dynamic heterogeneity at the segmental relaxation time scale since it biases the local composition toward a 1:1 ratio due to stoichiometric association.

Acknowledgment. The authors express their appreciation to the National Science Foundation, Polymers Program, for support of this research. We also thank Prof. Ralph Colby for very helpful discussions.

References and Notes

(1) Bershtein, V. A.; Egorov, V. M. *Differential Scanning Calorimetry of Polymers*; Ellis Horwood: Chichester, 1994.
(2) Runt, J. P. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P., Fitzgerald, J. J., Eds.; American Chemical Society: Washington, DC, 1997; Chapter 10.

(3) Zhang, S. H.; Jin, X.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 3636.
(4) Alegría, A.; Colmenero, J.; Ngai, K. L.; Roland, C. M. *Macromolecules* **1994**, *27*, 4486.
(5) Min, B.; Qiu, X. H.; Ediger, M. D.; Pitsikalis, M.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 4466.
(6) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
(7) Ngai, K. L.; Roland, C. M. *Macromolecules* **1995**, *28*, 4033.
(8) Roovers, J.; Toporowski, P. M. *Macromolecules* **1992**, *25*, 3454.
(9) Alvarez, F.; Alegría, A.; Colmenero, J. *Macromolecules* **1997**, *30*, 597.
(10) Arbe, A.; Alegría, A.; Colmenero, J.; Hoffmann, S.; Willner, L.; Richter, D. *Macromolecules* **1999**, *32*, 7572.
(11) Miller, J. B.; McGrath, K. J.; Roland, C. M.; Trask, C. A.; Garroway, A. N. *Macromolecules* **1990**, *23*, 4543.
(12) Chung, G. C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 964.
(13) Pathak, J. A.; Colby, R. H.; Floudas, G.; Jérôme, R. *Macromolecules* **1999**, *32*, 2553.
(14) Cendoya, I.; Alegria, A.; Alberdi, J. M.; Colmenero, J. *Macromolecules* **1999**, *32*, 4065.
(15) Le Menestrel, C.; Kenwright, A. M.; Sergot, P.; Lauprêtre, F.; Monnerie, L. *Macromolecules* **1992**, *25*, 3020.
(16) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(17) Pathmanathan, K.; Johari, G. P. *J. Polym. Sci., Polym. Phys.* **1987**, *25*, 379.
(18) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363.
(19) Takeno, H.; Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1996**, *29*, 2440.
(20) Shimizu, H.; Horiuchi, S.; Kitano, T. *Macromolecules* **1999**, *32*, 537.
(21) Urakawa, O.; Fuse, Y.; Hori, H.; Tran-Cong, Q.; Yano, O. *Polymer* **2001**, *42*, 765.
(22) Zetsche, A.; Fisher, E. W. *Acta Polym.* **1994**, *45*, 168.
(23) Katana, G.; Fischer, E. W.; Hack, T.; Abetz, V.; Kremer, F. *Macromolecules* **1995**, *28*, 2714.
(24) Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J. Chem. Phys.* **1996**, *105*, 3777.
(25) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33*, 5278.
(26) Leory, E.; Alegeria, A.; Colmenero, J. *Macromolecules* **2002**, *35*, 5587.
(27) Salaniwal, S.; Kant, R.; Colby, R. H.; Kumar, S. K. *Macromolecules* **2002**, *35*, 9211.
(28) Zhang, S. H.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 9403.
(29) Zhang, S. H.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 8478.
(30) Tomlin, D. W.; Roland, C. M. *Macromolecules* **1992**, *25*, 2994.
(31) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
(32) McClellan, A. L. *Tables of Experimental Dipole Moments*; Rahara Enterprises: El Cerrito, CA, 1974.
(33) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966**, *14*, 99.
(34) Havriliak, S.; Havriliak, S. J. In *Dielectric Spectroscopy of Polymeric Materials*; Runt, J. P., Fitzgerald, J. J., Eds.; American Chemical Society: Washington, DC, 1997; Chapter 6.
(35) Asano, A.; Eguchi, M.; Shimizu, M.; Kurotsu, T. *Macromolecules* **2002**, *35*, 8819.
(36) Gestoso, P.; Brisson, J. *Polymer* **2001**, *42*, 8415.
(37) Rinderknecht, S.; Brisson, J. *Macromolecules* **1999**, *32*, 8509.
(38) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.
(39) Painter, P. C.; Veytsman, S.; Kumar, S.; Graf, J. F.; Xu, Y.; Coleman, M. M. *Macromolecules* **1997**, *30*, 932.
(40) Painter, P. C.; Park, Y.; Coleman, M. M. *J. Appl. Polym. Sci.* **1998**, *70*, 1273.
(41) Ngai, K. L.; Roland, C. M. *Macromolecules* **1993**, *26*, 6824.
(42) Colby, R. H. *Phys. Rev. E* **2000**, *61*, 1783.
(43) Erwin, B. M.; Colby, R. H. *J. Non-Cryst. Solids* **2002**, *307*, 225.
(44) Rubinstein, M.; Semenov, A. N. *Macromolecules* **2001**, *34*, 1058.
(45) Jiang, M.; Li, M.; Xiang, M. L.; Zhou, H. *Adv. Polym. Sci.* **1999**, *146*, 121.

MA034501R