Suppression of the Dielectric Secondary Relaxation of Poly(2-vinylpyridine) by Strong Intermolecular Hydrogen Bonding

Shihai Zhang, Paul C. Painter, and James Runt*

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

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ABSTRACT: The secondary relaxation of poly(2-vinylpyridine) (PVPy) in a complex and blends with poly(4-vinylphenol) (PVPh) was studied by broadband dielectric spectroscopy. The polymer complex can be obtained by mixing PVPh and PVPy in methyl ethyl ketone as a result of the very strong hydrogen bonding between two polymers, and it has a glass transition temperature higher than that of either component. The secondary relaxation of PVPy is clearly suppressed in the complex, and it is found that the reduction of its dielectric relaxation strength is approximately proportional to the intermolecular hydrogen bonding fraction. In addition, the relaxation time of unassociated PVPy side groups is also slowed down by about 1 decade compared to that of the neat PVPy. Homogeneous PVPh/PVPy blends can be achieved if the polymers are mixed in *N*,*N*-dimethylformamide. However, the degree of intercomponent hydrogen bonding is much lower in the blends, and therefore the suppression of the PVPy secondary relaxation is not as significant as in the complex. Furthermore, by comparing with results reported earlier, it is concluded that the stronger the intermolecular hydrogen bonding, the more significantly it influences the secondary relaxation of the proton-accepting component.

Introduction

Although the viscosity increases rapidly and structural (segmental) relaxations are dramatically retarded approaching the glass transition temperature (T_g) in glass-formers, relaxations at smaller length scale are still able to occur below T_g in the solid state. One of these is the secondary β relaxation, which is faster than the primary segmental relaxation.[1−4]

In polymers, the secondary relaxation process can originate from side group rotation around the bond connecting it to the backbone or localized crankshaft motions of four chemical bonds in the backbone.[5,6] At temperatures below T_g, chains are in a nonequilibrium state, and secondary relaxation can take place in loosely packed regions due to frozen-in density fluctuations, i.e., the so-called “islands of mobility”.[1] The observed secondary relaxation time distribution is usually very broad, and its intensity decreases with decreasing temperature. Two scenarios have been proposed to interpret this behavior: only chains in the low-density regions can relax with different rates due to their different local environments, or all chains are able to relax with a nearly temperature-independent amplitude.[1] This relaxation is of importance since it influences material properties in a variety of ways, e.g., dissipating impact energies and facilitating gas permeation below T_g.

Although mixing with a miscible polymer or solvent can significantly influence the segmental relaxation through changing T_g, its effect on the secondary relaxation is not obvious, and distinct behavior has been observed in different systems. In blends of polystyrene (PS) with poly(vinyl methyl ether) (PVME), the secondary relaxation of PVME is essentially located at the same frequency as that in neat state, with an intensity proportional to its concentration.[7] Similar behavior has also been observed in polyisoprene/poly(vinylethylene) (PI/PVE)[8] and bisphenol A polycarbonate/tetramethylbisphenol A polycarbonate (BPA-PC/TMBPA-PC) blends,[9] although contradictory findings have been reported for the latter system.[10,11] Since the secondary relaxation involves a length scale smaller than 1 nm, blending with a second molecule may not modify chain environment and conformations at such a local level. However, suppression of sub-T_g relaxations has indeed been observed for several polymer blends and plasticized polymers (mostly involving polycarbonate as one component), i.e., the so-called “antiplasticization” effect resulting from a negative change in density of mixing and/or strong intermolecular interactions.[12−16] Speeding up of the secondary relaxation has also been observed in plasticized TMBPA-PC and interpreted by the coupling model.[17−19]

Recently, the influence of hydrogen bonding on the secondary relaxation has been studied by our group using broadband dielectric spectroscopy (DRS), and several interesting features have been uncovered. Specifically, in blends of poly(4-vinylphenol) (PVPh) with poly(ethyl methacrylate) (PEMA),[20] although a portion of the carbonyl groups of PEMA are hydrogen bonded with PVPh, the secondary β relaxation of PEMA, originating from hindered side group rotation, is only slightly slowed down (less than 0.5 decades) by the presence of 40% PVPh. It was further found that the dielectric relaxation strength ($\Delta\epsilon$) of the β process in poly(methyl methacrylate) (PMMA) is nearly proportional to its concentration in blends with PVPh, unambiguously demonstrating that hydrogen bonding with PVPh does not significantly influence the side group rotating ability of PEMA and PMMA.[21] However, the dielectric β relaxation of poly(vinyl methyl ether) (PVME) can be significantly retarded (~2 decades) by hydrogen bonding with PVPh or the low molecular weight model compounds 4-ethylphenol (EPh) and bis(4-hydroxyphenyl)methane (BPM).[22,23] The different relaxation behavior

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

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Table 1. Glass Transition Temperatures of the Dielectric Samples

PVPy/PVPh	PVPy	10/90	40/60	complex	PVPh
T_g (°C)	100	116	144	176	173
ΔC_p (J/(K g))[a]	0.35	0.47	0.46	0.56	0.29

[a] Defined as the heat capacity difference between the liquid and glassy states.

of the hydrogen-bonded side groups in the above examples can be interpreted by considering their interaction strengths: the hydrogen bond in PVME mixtures is ~22 kJ/mol, stronger than the ~16 kJ/mol in PMMA or PEMA blends. This leads to a natural question: can the secondary relaxation be completely suppressed if the hydrogen bonding is sufficiently strong?

It has been shown that hydrogen bonding between the −OH in PVPh and nitrogen in poly(2-vinylpyridine) (PVPy) is much stronger than those mentioned above.[24,25] In fact, polymer complexes can be obtained by mixing PVPh and PVPy in methyl ethyl ketone (MEK) or tetrahydrofuran (THF). In the present study, we report our dielectric study of the β relaxation of PVPy in its blends and complexes with PVPh. Comparison with previous results will also be presented to provide a correlation between the interaction strength and its ability to modify the β relaxation.

Experimental Section

PVPh was purchased from Aldrich, Inc. (reported $M_w = 21\,000$ and $M_w/M_n = 2.5$), and PVPy from Scientific Polymer Products Inc. (reported $M_w = 76\,000$ and $M_w/M_n = 2.0$).

Two groups of samples were studied. The first one was the polymer complex, obtained by mixing 5% MEK solutions of PVPh and PVPy. A precipitate formed immediately, indicative of complexation. The precipitate was washed with acetone several times and dried in a vacuum oven at 80 °C for over 1 week. Films of the complex and neat PVPy were obtained by compressing at 220 and 200 °C, respectively. Although the feed ratio of PVPh/PVPy is 50/50 by mol % of repeat units (OH/N), ^{1}H NMR demonstrated that the complex has a different composition 40/60 (43/57 by weight), suggesting that some PVPh chains were washed out by acetone and a few PVPy functional groups remain unassociated.

The second group of samples were polymer blends, which were obtained by mixing PVPh and PVPy in *N*,*N*-dimethylformamide (DMF), in which homogeneous solutions were obtained. Most DMF was evaporated on a hot plate, and then the samples were held in a vacuum oven at 70 °C for over 5 weeks and at 120 °C for another 4 days to remove all residual solvent. All films are optically transparent, and gold was sputtered to promote electrical contact with the instrument electrode.

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 $\sim T_g + 80$ °C 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 °C.

Samples for DSC were cut from the DRS samples immediately before dielectric experiments. T_g was measured using a TA Q100 instrument. T_g was taken as the midpoint of the heat capacity change at a 10 °C/min heating rate.

Results and Discussion

Both the complex and blends have single T_g's, demonstrating global miscibility. T_g's of all samples are listed in Table 1. It is worth pointing out that the complex has a T_g of 176 °C, which is higher than those of the components (100 and 173 °C for PVPy and PVPh, respectively), demonstrating that the strong hydrogen bonding between PVPy and PVPh produces a network with extremely high apparent molecular weight.

Since the hydrogen bond between PVPh and MEK is much weaker than that between PVPh and PVPy, PVPh preferably associates with PVPy to form the complex in MEK solution, which precipitates immediately as a result of its network structure. When DMF is used as the solvent, it competes with PVPy to form hydrogen bonds with comparable strength. Therefore, the polymer complex is not formed in DMF. Although miscible blends can still be obtained in DMF, the degree of intercomponent hydrogen bonding was lower than that in the corresponding complex with the same composition. This is supported by the relatively low T_g observed in the 40/60 blend (144 °C), which is 32 °C lower than the T_g of the complex with 43/57 composition.

Dielectric Relaxations of Neat Polymers. As observed in other homopolymers, the segmental relaxation of PVPy occurs above its T_g and exhibits non-Arrhenius behavior. Its relaxation strength, $\Delta\epsilon_\alpha$, is ~5, significantly higher than the value of 2−3 observed for many homopolymers. A secondary β process is observed at ~200 kHz and 60 °C. With decreasing temperature, it shifts to lower frequencies following an Arrhenius form, and the relaxation strength is weakened at the same time. Its relaxation time distribution is extremely broad, with a full width at half peak height of ~7 decades at 0 °C, and it becomes broader at lower temperatures. The observed PVPy β relaxation is about 8 decades slower than the α process at T_g. Considering its simple chemical structure, the β relaxation of PVPy likely arises from pyridine group rotation around the C−C bond connecting it with the backbone. Dielectric spectra of PVPy are presented in Figure 1. It should be noted that the β relaxation of PVPy is also very strong, with a peak intensity, ϵ''_{max}, of ~0.26 at 80 °C, which compares with ~0.025 for PVME at −110 °C with $\tau_{max}(\beta)$ of 5×10^{-7} s. The high dielectric relaxation strength of PVPy likely results from its large dipole moment, ~2 D (for the saturated repeat unit 2-ethylpyridine), at room temperature.[26]

The secondary β relaxation of PVPh is about 5 decades faster than that of PVPy at the same temperature; e.g., it occurs at ~1 MHz at −40 °C, while the β process of PVPy takes place at around 15 Hz at this temperature. In addition, $\Delta\epsilon_\beta$(PVPh) is only ~30% of $\Delta\epsilon_\beta$(PVPy) (Figure 2). Therefore, the observed dielectric response is dominated by PVPy in the temperature range of interest (−60 to 60 °C).

Secondary Relaxations in the Complex and Blends. Figure 3 presents the dielectric loss spectra of the 10/90 and 40/60 PVPh/PVPy blends at temperatures where the secondary relaxation of PVPy can be observed in the accessible frequency window. In the blend with 10% PVPh, the β process of PVPh is very weak and cannot be observed. The secondary relaxation of PVPy occurs at nearly the same frequency, but with lower intensity, compared to that in neat PVPy. This is a result of dilution from blending and also from suppression of the relaxation by strong hydrogen bonding. In the blend with 40% PVPh, the dielectric loss spectra exhibit dramatic broadening and a shoulder can be identified at lower frequency, suggesting a bimodal distribution. The ϵ''_{max} of the 40/60 blend is about 40% of that of neat PVPy.

More significant suppression of the PVPy β process is found in the PVPh/PVPy complex (Figure 4) with 43/

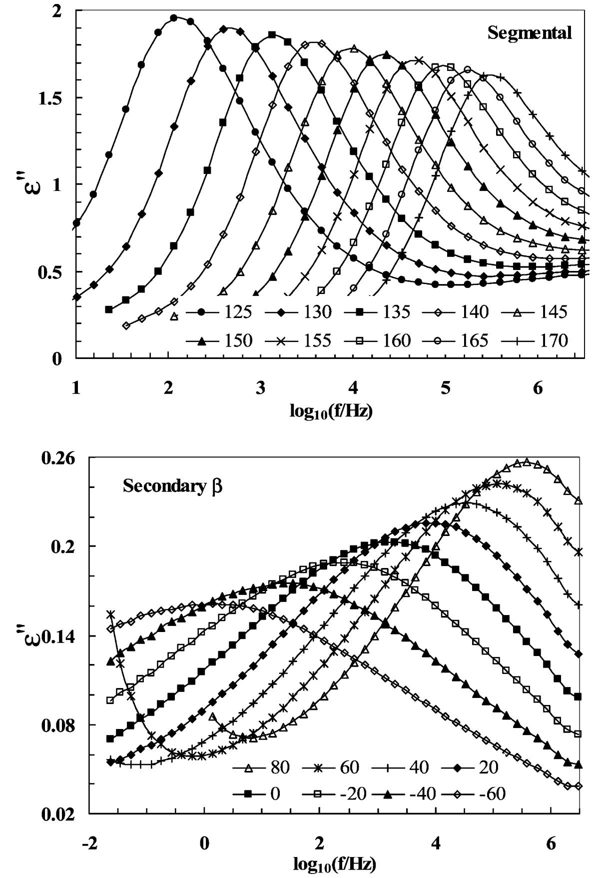

Figure 1. Dielectric loss spectra of PVPy at selected temperatures (in °C). The dc conduction has been removed from the segmental relaxation spectra.

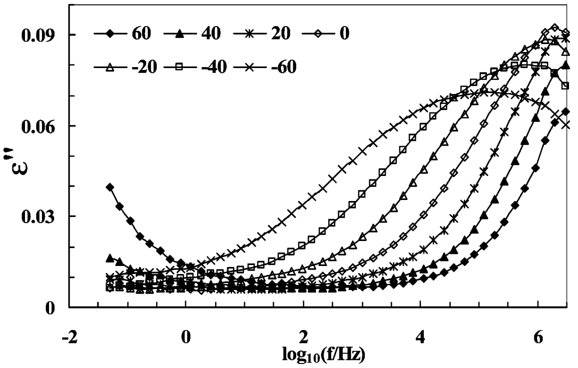

Figure 2. Dielectric loss spectra of the secondary relaxation of PVPh (temperatures in °C).

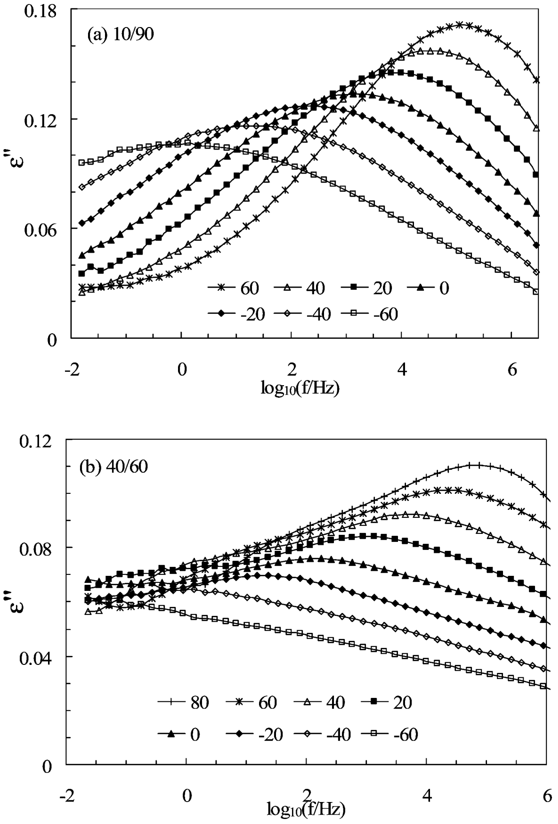

Figure 3. Dielectric loss spectra of (a) 10/90 and (b) 40/60 PVPh/PVPy blends (temperatures in °C).

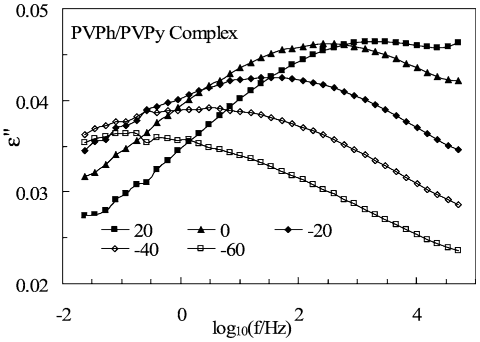

Figure 4. Dielectric loss spectra of the secondary relaxation of the PVPh/PVPy complex (temperatures in °C).

57 composition. Three features can be immediately identified from the figures. First, the secondary relaxation of PVPy is suppressed by the addition of PVPh. The peak intensity reduces to about ∼20% of PVPy at the same temperature. Second, the relaxation time distribution becomes much broader. Third, although the complex is composed of 43% (by weight) PVPh, Figure 4 does not exhibit any significant relaxation process at the original peak location of β(PVPh), suggesting that the secondary relaxation of PVPh is completely suppressed. This is rather surprising considering that the β relaxation is well-defined in neat PVPh, in which intracomponent −OH···OH hydrogen bonding dominates.

The real part of the dielectric permittivity ϵ^*, ϵ', exhibits trends similar to those observed in the dielectric loss ϵ''. The dielectric relaxation strength $\Delta\epsilon$ can be equivalently obtained from both ϵ' and ϵ'' through[5]

$$\Delta\epsilon = \epsilon_{\mathrm{R}} - \epsilon_{\infty} = \frac{2}{\pi}\int_{-\infty}^{\infty} \mathrm{d}(\ln \omega)\epsilon''(\omega) \tag{1}$$

where ϵ_∞ and ϵ_{R} are the unrelaxed and relaxed ϵ' at very high and low frequency, respectively, $\omega = 2\pi f$. For the β relaxation, ϵ_∞ and ϵ_{R} are defined as ϵ' at frequencies where the β relaxation begins and finishes, respectively. Figure 5a shows the ϵ' spectra at −20 °C. The difference between ϵ' at low and high frequency ($\Delta\epsilon$) clearly increases in the sequence: the complex, the 40/60 blend, the 10/90 blend, neat PVPy. This is consistent with the results obtained from the ϵ'' spectra. However, it should be pointed out that the ϵ' spectra have been vertically shifted for comparison purposes. In the original spectra, the unrelaxed dielectric constant ϵ_∞ is somewhat larger for the 10/90 and 40/60 blends than for neat PVPy. This may be a consequence of some residual DMF, whose relaxations can occur at much higher frequencies and

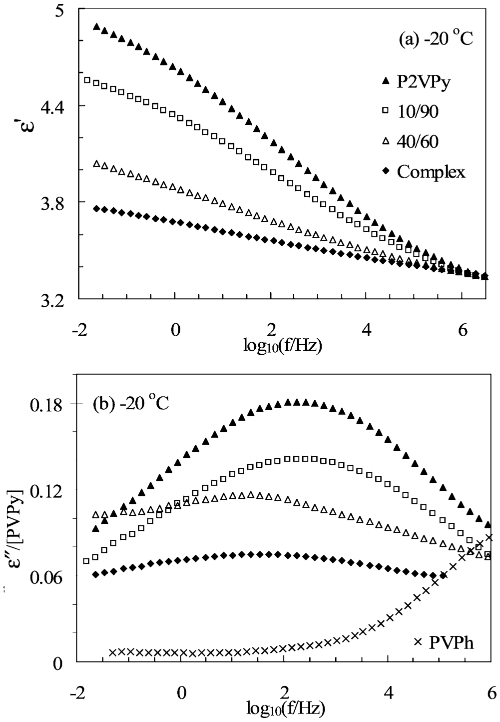

Figure 5. Comparison of the dielectric spectra of different mixtures at −20 °C. For comparison, the ϵ' spectra of the complex and 10/90 and 40/60 blends are vertically shifted by 0.29, −0.27, and −0.44, respectively. The ϵ'' spectra have been normalized by the concentration of PVPy in each sample.

contribute to the measured ϵ_∞. However, the complex has a smaller ϵ_∞ than PVPy, suggesting that some faster relaxation processes are also suppressed in the former. Nevertheless, since it is much faster than the PVPy β relaxation, this does not challenge the validity of the current analysis.

Dilution of PVPy by blending certainly contributes to the reduction of $\Delta\epsilon_\beta$ in the blends and complex; however, it cannot fully account for the decrease, as demonstrated in Figure 5b in which the loss curves at −20 °C are normalized by PVPy concentration. If hydrogen bonding with PVPh did not influence the β relaxation of PVPy, the blends and complex should have the same $\Delta\epsilon_\beta$ as that of neat PVPy after concentration normalization. Obviously, their relaxation strengths are significantly weaker than expected from dilution alone, and we confidently conclude that the secondary relaxation of PVPy is suppressed by hydrogen bonding with PVPh.

To quantify the suppression, $\Delta\epsilon$, together with the mean relaxation time $\tau_{\max}$ and the distribution shape parameters a and b, can be obtained by fitting the experimental spectra with the phenomenological Havriliak−Negami (HN) equation[5]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon(\omega) = \epsilon_\infty - i\,\frac{\sigma_0}{(\epsilon_{\mathrm{v}}\omega)^s} + \frac{\Delta\epsilon}{[1 + (i\tau_{\mathrm{HN}}\omega)^a]^b} \tag{2}$$

Here ϵ_{v} is the vacuum permittivity, σ_0 is the dc conduction constant with units of S/cm, and the exponent s ($0 < s \le 1$) characterizes the conduction process. The characterization time τ_{HN} is related to $\tau_{\max}$ by[5]

$$\tau_{\max} = \tau_{\mathrm{HN}}\left[\sin\frac{\pi ab}{2(b+1)}\Big/\sin\frac{\pi a}{2(b+1)}\right]^{1/a} \tag{3}$$

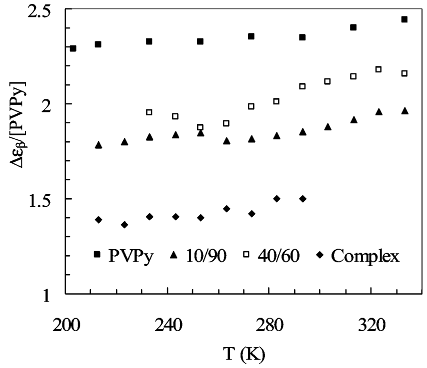

Figure 6. Dielectric relaxation strength of the β process obtained by HN curve fitting the loss spectra, normalized by the concentration of PVPy.

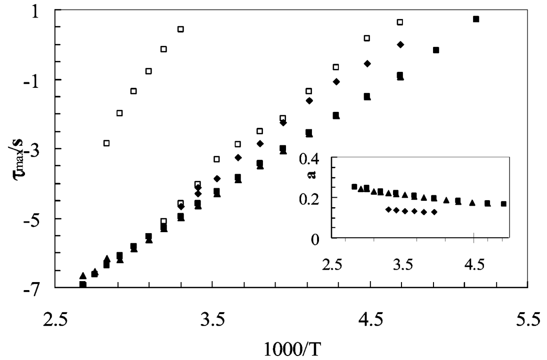

Figure 7. Relaxation times of the PVPy β process in different samples. Labels are the same as in Figure 6. PVPy (solid squares) and the 10/90 blend (solid triangles) have nearly identical relaxation times, and they are overlapped in the figure at most temperatures. Two processes (open squares) are used to fit the secondary relaxation for the 40/60 blend. The inset shows the distribution shape parameter a as a function of temperature, with larger a representing a narrower distribution. The shape parameter $b = 1$ for data shown in the inset, implying a symmetrical distribution.

For neat PVPy, the 10/90 blend, and the complex, their β relaxations can be fitted with one HN function, and the shape parameter b was found to be 1 at most temperatures, indicating a symmetric Cole−Cole distribution. For the 40/60 blend, a shoulder emerges on the low-frequency side and two HN functions must be used to reasonably fit the data. The calculated $\Delta\epsilon$ is presented in Figure 6 after normalized by PVPy concentration, in which data for the 40/60 blend represent the total relaxation strength of the two processes. The normalized relaxation strengths are still significantly smaller than that of neat PVPy, again supporting the suppression of the PVPy β relaxation by blending with PVPh.

The relaxation times are provided in Figure 7. The 10/90 blend has nearly the same $\tau_{\max}$ as that of PVPy with an activation energy $E_{\mathrm{a}} = 57$ kJ/mol and a prefactor $= 1.6 \times 10^{-15}$ s. Moreover, they also have identical shape parameters a, indicating similar relaxation time distributions at the same temperature (since $b = 1$ for both). Moreover, a decreases with decreasing temperature, indicative of a broader distribution. On the other hand, the β relaxation of PVPy in the complex is slower than that of neat PVPy. The relaxation time distributions of the complex and the 40/60 blend are significantly broader than PVPy and the 10/90 blend, as shown in Figures 5 and 7.

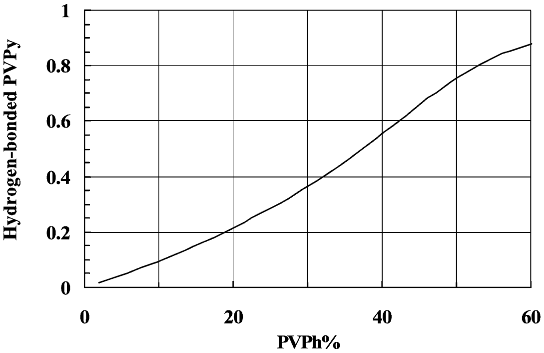

Figure 8. Calculated hydrogen-bonding fraction of PVPy at 25 °C. The calculation is performed following the methodology of Painter and Coleman[27] with $K_2^{\mathrm{Std}} = 21$, $K_B^{\mathrm{Std}} = 66.8$, $K_A^{\mathrm{Std}} = 1200$ and intramolecular screening factor $\gamma = 0.3$.

Influence of Hydrogen Bonding. An ideal polymer complex should consist of equal molar amounts of each component. In the PVPh/PVPy complex studied herein, however, the concentration of PVPy (~60 mol %) is higher than expected. Therefore, some of the PVPy side groups remain unassociated. It is desirable to know how many of these are hydrogen bonded with PVPh so that quantitative analysis can be performed to assess whether there is a correlation between $\Delta\epsilon_\beta$ and unassociated PVPy fraction. Unfortunately, traditional FTIR methodology cannot be applied to PVPy/PVPh, since the bands associated with −OH stretching are very broad and those associated with pyridine groups of PVPy cannot also be used for quantitative analysis. Nevertheless, the fraction of hydrogen bonds can be theoretically estimated if the self- and interassociation equilibrium constants are known. The equilibrium constants for PVPh hydrogen-bonded dimers (K_2^{Std}), multimers (K_B^{Std}), and PVPh−PVPy hydrogen bonding (K_A^{Std}) are approximately 21, 66.8, and 1200, respectively, as derived from model low molecular weight analogues at 25 °C.[25,27] Taking into account the intramolecular screening inherent to long chain polymers, the fraction of hydrogen-bonded PVPy is calculated as a function of PVPh concentration and given in Figure 8.

It is seen in Figure 8 that around 60% of the PVPy side groups in the complex are hydrogen bonded with PVPh in thermodynamic equilibrium. If we assume that only unassociated PVPy contributes to the observed dielectric β relaxation, the effective PVPy concentration in the complex is only ~23 wt % considering that only 40% of the original 57% PVPy are unassociated. As an example, $\Delta\epsilon_\beta$ is 2.3 for PVPy at −20 °C, which leads to a theoretical relaxation strength of 0.53 in the complex; the experimental value, however, is 0.8. Although the experimental $\Delta\epsilon_\beta$ is larger than the predicted value, it is still much smaller than 1.31, the theoretical strength assuming hydrogen-bonded PVPy also contributes to the secondary relaxation.

The relatively large $\Delta\epsilon_\beta$ in the complex can be explained by considering that the actual hydrogen-bonding fraction of PVPy may be lower than estimated for the equilibrium state. Hydrogen bonding between two functional groups has strict distance and relative orientation requirements, which cannot be reached without structural (segmental) relaxations. It is very difficult, if not impossible, for the complex to arrive at hydrogen-bonding equilibrium in the solid state, which is far below its T_g and structural relaxations are essentially frozen. In addition, since the polymer complex immediately precipitates as soon as two solutions are mixed, this may also kinetically prevent maximum intermolecular hydrogen bonding. Therefore, it is reasonable to conclude that hydrogen bonding with PVPh suppresses the β relaxation of PVPy, i.e., its side group rotation. In addition, it should be pointed out that although the unassociated pyridine groups are still able to rotate, their relaxation rate is significantly slowed down (about 1 decade) in the complex (Figure 7).

The 40/60 blend has a relatively large $\Delta\epsilon_\beta$, ~1.2−1.3 at 20 °C, which is significantly higher than the polymer complex having similar composition. This is likely a result of the lower degree of intermolecular hydrogen-bonding concentration in the former. DMF molecules preferably form hydrogen bonds with PVPh in the mixed solution. Although DMF is finally removed, the N atom of the pyridine does not have sufficient mobility to access the −OH group of PVPh to form hydrogen bonds in the solid state. This is strongly supported by its low T_g. To reiterate, T_g of the 40/60 blend is only 144 °C, 32 °C below that of the complex. The lack of PVPy−PVPh associations can therefore rationalize the relatively high $\Delta\epsilon_\beta$ in the 40/60 blend.

The unusual low-frequency broadening of the β relaxation time distribution in the miscible 40/60 blend (i.e., a bimodal relaxation time distribution) is quite surprising considering that the blend exhibits a single DSC T_g. We speculate that a possible explanation lies in the existence of some “quasi” hydrogen bonds. During the final stages of DMF evaporation, although the pyridine and hydroxyl groups cannot actively approach each other and adjust their positions to assume appropriate positions for strong hydrogen bond formation due to the gradual freezing of structural relaxations, in some domains they are still relatively close to each other and form some weaker (“quasi”) hydrogen bonds. Although these interactions are weaker than normal hydrogen bonds, the latter having optimized distance and orientation, they are nevertheless able to slow down the PVPy β process, just as occurs in PVME/PVPh blends. This slow relaxation process is more than 5 decades slower than the rotation of pyridine groups in neat PVPy.

As noted earlier, the secondary relaxation in the 10/90 blend maintains nearly the same character as that of neat PVPy. On the basis of theoretical estimates, it is predicted that around 10% of the pyridine groups are hydrogen bonded with PVPh, leading to $\Delta\epsilon_\beta$ ~1.9 at 20 °C if blending itself does not influence the secondary process of PVPy. The experiment yields $\Delta\epsilon_\beta \approx 1.7$, 10% smaller than expected. Nevertheless, considering the fact that PVPy and this blend have nearly the same mean β relaxation time and distribution, this small difference is attributed to the uncertainty in curve fitting and sample thickness. Furthermore, because the PVPh concentration in this blend is very low, there is stoichiometrically more PVPy available to form hydrogen bonds with PVPh, thermodynamic equilibrium can be achieved, and thus the relaxation time distribution is not broadened.

Comparison with Other PVPh Blends. As noted in the introductory section, we found previously that hydrogen bonding with PVPh does not influence the β relaxation of PMMA and PEMA in their blends but slows down the β process of PVME. It should be pointed out that although the secondary relaxation time distri-

Table 2. Activation Energies and Hydrogen Bonding Strengths with PVPh

	PEMA	PMMA	PVME	PVPy
E_a (kJ/mol)[a]	68	77	22	57
$-\Delta H_{HB}$ (kJ/mol)[b]	16	16	22	34
$\Delta\nu_{OH}$ (cm^{-1})[c]	140	140	215	319
effect	unchanged	unchanged	retarded	suppressed

[a] Activation energy of the β process of the proton-accepting polymer. [b] Enthalpy of hydrogen bonding. [c] Wavenumber shift of hydrogen-bonded PVPh hydroxyl stretching mode from that of the free phenolic hydroxyl groups. Larger $\Delta\nu_{HB}$ indicates stronger hydrogen bonding.

bution of PVME is significantly broadened at lower frequencies after blending with PVPh, the dielectric relaxation strength is approximately proportional to the global concentration of PVME. In the present study, it is suggested that association with PVPh suppresses the rotation of the pyridine units in PVPy. These diverse effects of hydrogen bonding demand a detailed comparison. Table 2 provides the activation energies and hydrogen-bonding strengths in the three different blends. It is clear that stronger intercomponent hydrogen bonding influences the secondary relaxation of the proton-accepting polymers more significantly. When the enthalpy of hydrogen bonding with PVPh increases from 16 kJ/mol for PMMA and PEMA, whose β relaxations are nearly unaffected, to 22 kJ/mol for PVME, the β process of the latter is retarded by ~2 decades. A $-\Delta H_{HB}$ of 34 kJ/mol with PVPh can effectively suppress the pyridine groups' rotation. This trend is consistent with the unchanged secondary dynamics observed in PVME/PS and PIP/PVE blends,[7,8] in which only weak van der Waals interactions are present. Although one might naively expect that a β process with larger activation energy would be more difficult to modify by strong interactions, this is not necessarily true as seen in Table 2, in which there is no correlation between E_a and the degree of modification, particularly considering the relatively large E_a of PVPy β process.

Furthermore, the suppression of the PVPy β process also suggests that the effective lifetime of the PVPh−PVPy hydrogen bond is much longer than the β relaxation time. Secondary relaxation in PVPy, specifically the rotation of the pyridine group, cannot take place without breaking the associated hydrogen bond because it will otherwise require simultaneous relaxation of PVPh hydroxyl groups. This cannot be achieved since cooperative relaxation of PVPh chains is impossible at temperatures far below T_g. The lifetime of the PVPh−PMMA (or PEMA) hydrogen bonds may be significantly shorter than their β relaxation time, so that side group rotation can readily occur during the open period of associated hydrogen bonds, sometimes even without any retardation. This is reasonable because stronger hydrogen bonding should result in longer lifetimes than weaker ones. A slowdown of the β relaxation can be observed when the hydrogen bond lifetime is comparable to the corresponding β relaxation time. If the former is slightly shorter than the latter, relaxation can occur but with additional friction; for the opposing situation, the side group attempts several times before the associated hydrogen bond breaks, and its actual relaxation time may equal the lifetime of the association at the same temperature.

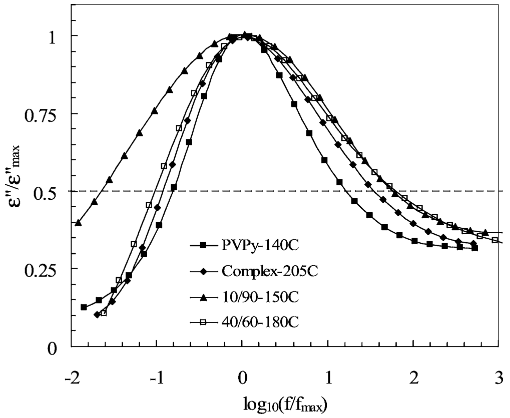

Figure 9. Segmental relaxations of different samples. For comparison, dc conduction is removed and the spectra are normalized by ϵ''_{max} and f_{max}. Temperatures are selected so that the samples have similar relaxation times, with peaks located around 1 kHz.

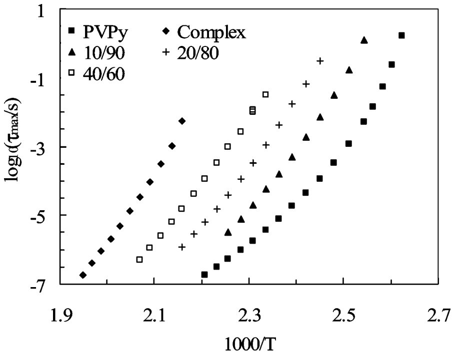

Figure 10. Segmental relaxation times of different samples as a function of reciprocal temperature.

Segmental Relaxations. Segmental dynamics in hydrogen-bonded polymer blends have been discussed in previous publications. In general, it is found that intercomponent hydrogen bonding can dampen concentration fluctuations and couple components' segmental relaxations; this is more clearly observed when they have very large T_g difference.[20,23,28−31] The 40/60 PVPh/PVPy blend and the complex exhibit similar behavior. Their relaxation time distributions are close to that of neat PVPy, suggesting insignificant dynamic heterogeneity (Figure 9). This is not surprising considering the very strong intermolecular interactions and the relatively small T_g difference (72 °C, much smaller than the 195 °C between PVPh and PVME). The 10/90 PVPh/PVPy blend, however, exhibits unusual low-frequency broadening of its segmental relaxation time distribution. This behavior is reminiscent of the broadening observed in PVPh/poly(vinyl ethyl ether) (PVEE) blends with low PVPh concentrations and likely results from the coexistence of associated and unassociated PVPy segments, with the former relaxing much slower than the latter.[28,30]

Segmental relaxations of all samples follow the well-known Vogel−Fulcher−Tammann (VFT) equation $\tau_{max} = \tau_0 \exp[B/(T - T_0)]$ (Figure 10).[32] Because of the strong dc conduction at high temperatures, the relaxation times approaching T_g cannot be resolved. The fragility,[33,34] defined as $m = \mathrm{d}\log(\tau_{max})/\mathrm{d}(T_{ref}/T)|_{T=T_{ref}}$, cannot be obtained if the reference temperature T_{ref} is defined at $\tau_{max} = 1$ s, due to the difficulty in extrapolating τ_{max} to T_{ref}. For comparison, the fragility at $\tau_{max} = 0.001$ s can be used, and it qualitatively increases from neat PVPy, to the 10/90 blend, 40/60 blend, and to the complex. This suggests that the intermolecular coupling in the complex is stronger than that in all other samples.

Summary

The secondary relaxations of PVPy in the complex and blends with PVPh were studied by broadband dielectric spectroscopy. The polymer complex is formed in methyl ethyl ketone solution since the MEK−PVPh hydrogen bonding is much weaker than the PVPy−PVPh interaction. The strong hydrogen bonding in the complex leads to a T_g of 176 °C, higher than that of both PVPh and PVPy. The PVPy β relaxation is suppressed in the complex, and the experimental $\Delta\epsilon_\beta$ is approximately proportional to the concentration of unassociated PVPy. This suggests that the PVPy β relaxation cannot take place once the groups are hydrogen bonded with PVPh.

By using DMF as the solvent, homogeneous PVPh/PVPy blends are obtained. The concentration of PVPh−PVPy hydrogen bonds is much lower than in the complex with similar composition. T_g of the 40/60 blend is 32 °C lower than that of the above complex (PVPh/PVPy = 43/57). Therefore, the 40/60 blend has a much larger $\Delta\epsilon_\beta$ than the complex. The 10/90 blend, on the other hand, maintains the same relaxation time and distribution as that of neat PVPy at the same temperature, with a relaxation strength proportional to the non-hydrogen-bonded PVPy content. The ability of PVPh to affect the β relaxation of the other component is found to be closely correlated with the intercomponent hydrogen-bonding strength by comparing the current results with those for PVPh blended with PMMA (or PEMA) and PVME.

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