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# Localized Cooperative Molecular Motion in Miscible Polymer Mixtures with Large Difference in Glass-Transition Temperatures

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ABSTRACT: An experimental study using dielectric spectroscopy measurements is made on molecular motions as functions of temperature and pressure of polystyrene (PS) and poly(vinyl methyl ether) (PVME) mixtures having large difference in glass transition temperatures. For mixtures with high concentration of PS, the largest loss peak and a shoulder at higher temperatures are observed. Our detailed analysis of molecular motion leads to the result that the former is not due to the α process of PVME-rich region arising from dynamic heterogeneity for miscible polymer mixtures, but due to local cooperative motion where favorable orientational motion of PVME is induced through a change in the environments formed by the PS matrix.

## 1. Introduction

Recently, it has been shown by numerous researchers that the dynamical asymmetry between constituent molecules is responsible for unique behaviors in various phenomena such as the phase separation process,[1] the relaxation process of concentration fluctuations within the one-phase region,[2] mixing behaviors of polymer mixtures in the one-phase region[3] or molecular motions such as the α process associated with glass transition,[4] and shear-induced phase separation.[5] Concerning the α process of miscible polymer mixtures with large difference in glass transition temperatures ($T_g$) where intermolecular interactions are weak, the existence of dynamic heterogeneity, i.e., two α processes irrespective of the miscibility (judged from the static measurements),[4] has been reported. Though several models such as thermal concentration models,[6] self-concentration models,[7] or a combination of these two[8] have been proposed for the dynamic heterogeneity, our understanding about it has still remained incomplete. For example, details of dynamics of each segment such as activation energy, temperature dependence of dielectric strength, and pressure change in the relaxation time (activation volume) do not appear to have been clarified.

In this work, we investigated molecular motions in polystyrene (PS) and poly(vinyl methyl ether) mixtures with a difference ($\Delta T_g \approx 127$ K) in glass transition temperature $T_g$ by performing dielectric spectroscopy (DS) measurements with particular attention paid to their temperature and pressure dependence. In many investigations in this area, efforts have been made almost exclusively to study the dielectric behavior of mixtures with high concentrations of PVME as a function of temperature. A few studies have been made on the pressure effects on the dielectric spectra for mixtures with high concentrations of PVME.[9−11] In this paper, an extensive study is made on the dielectric behavior of mixtures with high PS concentrations as a function of temperatures and pressures. Our particular intention in doing this is to clarify the dynamical properties of molecular motions in PS/PVME mixtures arising from cooperative local motions restricted in the surroundings formed by the PS matrix.

## 2. Experiments

**2.1. Sample Preparation and Characterization.** Protonated polystyrene (PS) was purchased from Aldrich Chemical Co. The number-averaged molecular weight $M_n$ and the polydisepersity indices $M_w/M_n$ were $1.8 \times 10^4$ and 1.07, respectively. Poly(vinyl methyl ether) (PVME) purchased from Aldrich Chemical Co. was fractionated by changing temperature in toluene/hexane solution. The PVME with $M_n = 2.0 \times 10^4$ and $M_w/M_n = 1.55$ was used for dielectric measurements. PS/PVME mixtures with compositions of PS/PVME 0/100, 30/70, 50/50, 70/30, and 80/20 in weight percent were prepared for dielectric measurements.

**2.2. Dielectric Spectroscopy (DS).** Measurements of DS were performed with a capacitance bridge by General Radio (GR-1615A) Co. in a frequency range of 0.03−100 kHz. For the 70/30 PS/PVME mixture we used a Hewlett-Packard impedance analyzer (HP4284A) together in order to measure dielectric spectra in the high-frequency range (up to 1 MHz). Pressure experiments were carried out up to 80 MPa for PS/PVME mixtures with compositions of 80/20 in weight percent, in which silicon oil was used as pressurizing liquid. The samples for dielectric measurements were freeze-dried by using benzene as a solvent in order to remove polar impurities such as moisture and afterward were melted at 70−90 °C in vacuo for ca. 2 or 3 days. Then the samples were melt-pressed into films at 90 °C in vacuo and sandwiched between two electrodes with three terminals. In the DS measurements, all the samples were vitrified at a constant cooling rate of 0.33 K/min because local motions in the glassy state are significantly affected by thermal history into vitrification.[12] As is well-known, this system has a lower-critical-solution-temperature-type phase diagram. The above sample preparation was performed at temperatures sufficiently lower than cloud points. All the measurements were carried out in the single-phase state. Since the dipole moment of PVME is much larger than that of PS, we will mainly observe the molecular motions of PVME in the dielectric measurements of PS/PVME mixtures.

## 3. Results

**3.1. DS Spectra.** Figure 1a shows the temperature dependence of the dielectric loss at frequency of 0.2 kHz for PS/PVME mixtures with compositions of 0/100, 30/70, 50/50, and 80/20 wt %/wt %. Though the dielectric loss data for 70/30 PS/PVME mixture are omitted for visual clarity, the behavior is similar to that of the 80/20 PS/PVME mixture. Three relaxation processes in neat PVME were observed in the temperature and frequency ranges covered in this study. A large dielectric loss peak observed at about 263 K for neat PVME is due to the α process,

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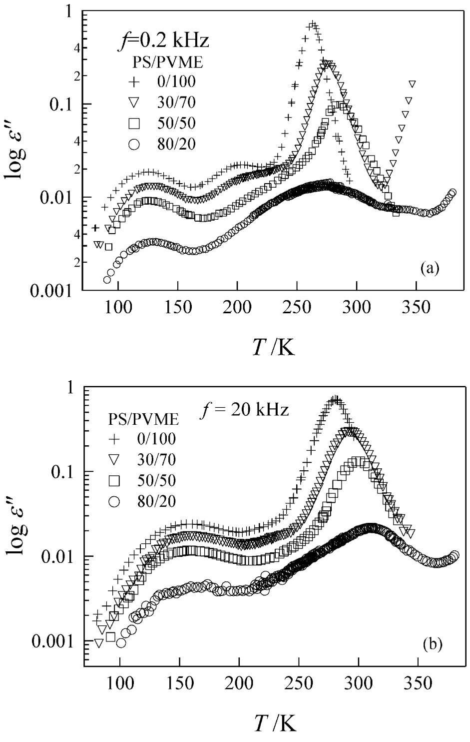

**Figure 1.** Temperature dependence of dielectric loss at (a) $f = 0.2$ kHz and (b) $f = 20$ kHz.

which is associated with the glass transition, while two peaks observed at about 200 and 120 K are due to the local modes of motions in the glassy state. We designate the peak observed around 200 K as the $\beta_1$ process and the peak observed at about 120 K as the $\beta_2$ process. The peak temperature of the dielectric loss in the $\beta_2$ process of all the mixtures is almost the same as that of neat PVME, though the magnitudes of the dielectric loss peaks decrease with decreasing content of PVME by the dilution effect. On the other hand, the behaviors of the $\beta_1$ process and α process depend largely on the composition. For 30/70 and 50/50 PS/PVME mixtures, the peak temperature in the α process shifts to higher temperature. The shift of the loss peak toward high temperature corresponds to the shift of the glass transition temperature of the mixture.[13] For the PS/PVME 50/50 mixture, a distinct peak observed is only that of the α process other than that of the $\beta_2$ process, although the dielectric loss in the temperature range of 200−250 K appears to broadly increase, which suggests some existence of the $\beta_1$ process. For the 80/20 PS/PVME mixture, a large peak at 275 K and a shoulder at 345 K were observed. The steep increase of dielectric losses at temperatures higher than 320 K for the 30/70 PS/PVME mixture and at temperatures higher than 365 K for the 80/20 PS/PVME mixture is due to conductivity losses. The loss peak of the $\beta_1$ process is not well-defined in the higher frequency (Figure 1b).

Figure 2a presents dielectric loss spectra in the $\beta_2$ process region for the 50/50 PS/PVME mixture. The dielectric loss spectra have a broad and symmetrical peak against a logarithmic scale of frequency. Figure 2b presents the frequency dependence of the dielectric loss in the $\beta_1$ process region for the PS/PVME 30/70 mixture. In this figure, at low temperatures, an increase of dielectric loss is observed at high frequencies due to the low-frequency tail of the $\beta_2$ loss peak. On the other hand, at high temperatures, an upturn of dielectric loss is observed at low frequencies, which is due to the tail of the α process. Figure 2c shows a plot of dielectric loss vs logarithmic frequency for the α process of neat PVME at various temperatures. The dielectric spectra have an asymmetrical shape against logarithmic frequency, broader at high frequencies than at low frequencies. The peak position shifts considerably toward the high-frequency side with a slight increase of temperature in comparison with the $\beta_1$ or $\beta_2$ processes.

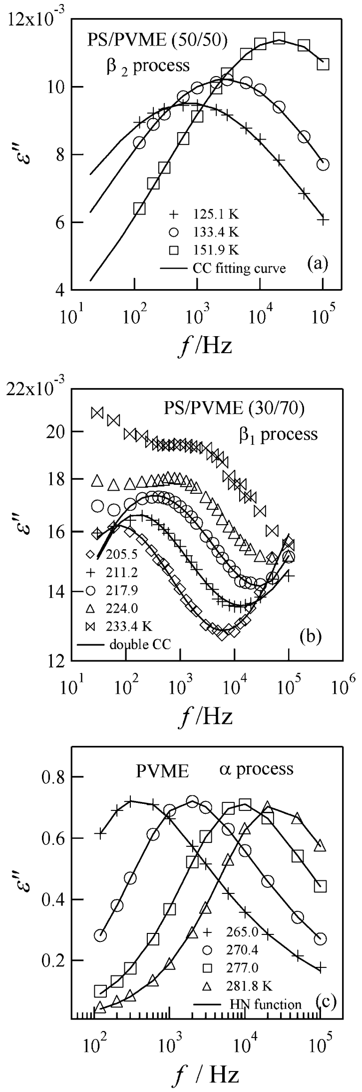

**Figure 2.** Frequency dependence of the dielectric loss. (a) $\beta_2$ process for the 50/50 PS/PVME mixture. Solid lines represent the Cole−Cole function fitted to the spectra data. (b) $\beta_1$ process for the 30/70 PS/PVME mixture. (c) α process for neat PVME. Solid lines represent the Haviriliak−Negami function fitted to the spectral data.

**3.2. Local Motions ($\beta_1$ and $\beta_2$ Processes) in Low-Temperature Regime.** First, let us analyze the loss peak ($\beta_2$ process) observed in the low-temperature regime at about 120 K at $f = 0.2$ kHz. For this purpose, we carried out the fitting procedure to the spectra with the Cole−Cole (CC) function which has well-described dielectric spectra of the localized $\beta$ process:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^a} \qquad (1)$$

with the complex dielectric constant $\epsilon^*(\omega) = \epsilon' - i\epsilon''$, where $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ is the relaxation strength. $\epsilon_0$ and $\epsilon_\infty$ are the dielectric constant at the low-frequency limit and at the high-frequency limit, respectively. α is a parameter which characterizes a distribution of the relaxation time, $\omega$ the angular frequency with the relation $f = \omega/2\pi$, and $\tau$ the relaxation time of the process under investigation. The solid curves in Figure 2a represent the curves fitted with the CC function, which are

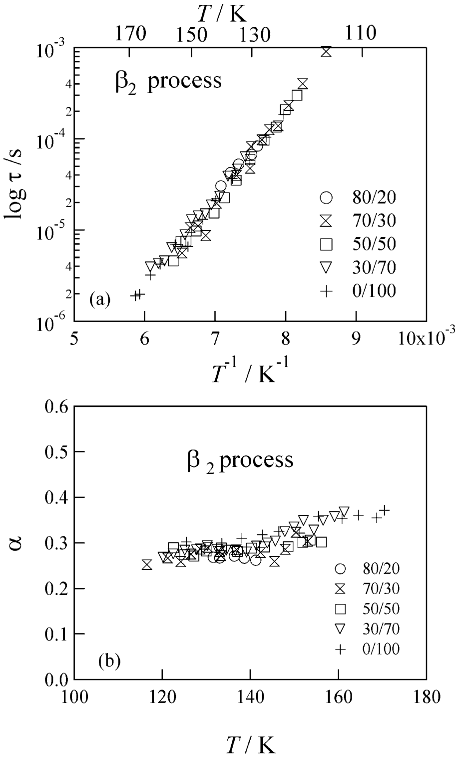

**Figure 3.** (a) Arrhenius plots of the $\beta_2$ process. (b) The distribution parameter α of the $\beta_2$ process as a function of temperature.

consistent with the dielectric loss data. In the fitting procedure, $\tau$, $\Delta\epsilon$, and α were obtained at respective temperatures. In Figure 3a we show a plot of log $\tau$ against reciprocal temperature (Arrhenius plot) for various mixtures. The relation between log $\tau$ and reciprocal temperature is linear for all the systems, and the locations and slopes are hardly affected by blending PS. This result is consistent with that by Cendoya et al. with dielectric spectroscopy.[14] We estimated the activation enthalpy $H^*$ of the relaxation process from the slope in Figure 3a:

$$H^* = R\frac{\partial \ln \tau}{\partial (1/T)} \tag{2}$$

where $R$ is the gas constant and $T$ is absolute temperature. $H^*$'s estimated thus are in the range of 15−21 kJ/mol.

The temperature dependence of α is shown in Figure 3b. The α's show almost the same values for all the system investigated, indicating the distribution of the motion is hardly affected by blending. Thus, the $\beta_2$ process is almost independent of blending PS in nature. The quantity $\Delta\epsilon$ slightly increases with increasing temperature, suggesting that the $\beta_2$ process has a thermally activated character.

As shown in Figure 2b, the $\beta_1$ peaks are affected by low-frequency tails of the $\beta_2$ process at low temperature and by high-frequency tails of the α process at high temperature. Therefore, they cannot be easily analyzed with a single Cole−Cole function. We tried to fit the dielectric loss data in the former region with a double Cole−Cole function under the assumption that the dielectric loss data can be described by the additive $\beta_1$ process and $\beta_2$ process. However, since in this procedure we have too many fitted parameters with two functions, the parameters obtained have extraordinary values. Therefore, we also tried to reduce fitted parameters by extrapolating the temperature dependence of $\Delta\epsilon$ in the $\beta_2$ process estimated in the temperature region where the $\beta_2$ peaks could be observed to the temperature region in the $\beta_1$ process; i.e., in the fitting procedure with two Cole−Cole functions we used the extrapolated values for $\Delta\epsilon$ of the $\beta_2$ process and fixed it. Since use of extraporated values for log $\tau$ or/and α in $\beta_2$ process resulted in unsatisfactory fits, we dealt with them as adjustable parameters in the procedure. Though the above method contains errors due to extrapolation, we believe that it is proper to obtain approximate values of $\tau$ or $\Delta\epsilon$ for the $\beta_1$ process. Furthermore, otherwise we fitted the spectra with a single Cole−Cole function by eliminating the data in both ends of frequencies under assumption that dielectric loss has a symmetric shape against a scale of logarithmic frequency. Since this procedure neglects the magnitude of dielectric loss due to low-frequency tail of the $\beta_2$ process or that due to the high-frequency tail of the α process, $\Delta\epsilon$ obtained should be overestimated. Therefore, the $\Delta\epsilon$ so obtained may be regarded as the upper-bound value (Figure 4).

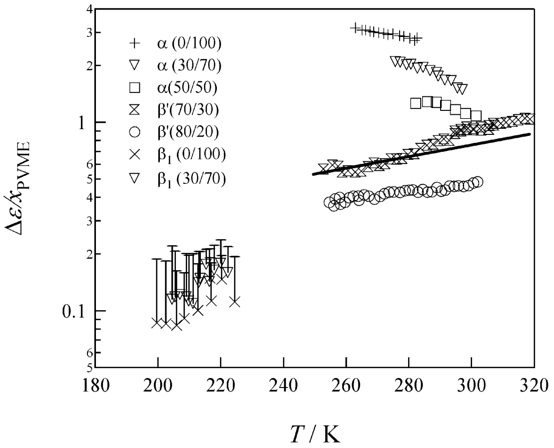

**Figure 4.** Dielectric strength $\Delta\epsilon$ reduced by mole fraction of monomer unit of PVME as a function of temperature for α, $\beta_1$, and $\beta'$ processes.

**3.3. Molecular Motions in High-Temperature Regime.** As mentioned above, the dielectric loss spectra in the α process have an asymmetrical shape. Therefore, their dielectric loss data were analyzed with the Havriliak−Negami (HN) function

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^a]^\gamma} \tag{3}$$

where $\tau_{HN}$ is the characteristic relaxation time. Here, the quantities α and $\gamma$ are parameters characterizing the shape of the curve: for $f \ll f_m$ and $f \gg f_m$, the function have power laws with exponents of α and $-\alpha\gamma$, respectively, where $f_m$ is the frequency at which dielectric loss spectra have peaks. For $\gamma = 1$, eq 3 reduces to the CC function, eq 1. In Figure 2c, the curves well fitted to the HN function correspond to the dielectric loss data in the α process for neat PVME. On the other hand, the loss spectra with the large peak for 70/30 and 80/20 PS/PVME mixtures could be represented well by the CC function. Hereafter, we designate the motions based upon the large loss peak for 70/30 and 80/20 PS/PVME mixtures as the $\beta'$ process.

In Figure 4 we show the temperature dependence of $\Delta\epsilon$ reduced by the mole fraction of monomer unit of PVME with respect to α processes, $\beta_1$ process, and $\beta'$ process. The quantity $\Delta\epsilon/x_{PVME}$ in the α process is found to decrease with increase of PS content. Here it is important to note that the $\Delta\epsilon$ for the $\beta_1$ process for neat PVME and 30/70 PS/PVME mixtures or the $\beta'$ process of 70/30 and 80/20 PS/PVME mixtures increases with increase of temperature, while those for the α process for neat PVME, 30/70 PS/PVME, and 50/50 PS/PVME mixtures decrease with increasing temperature. The latter reflects the fact

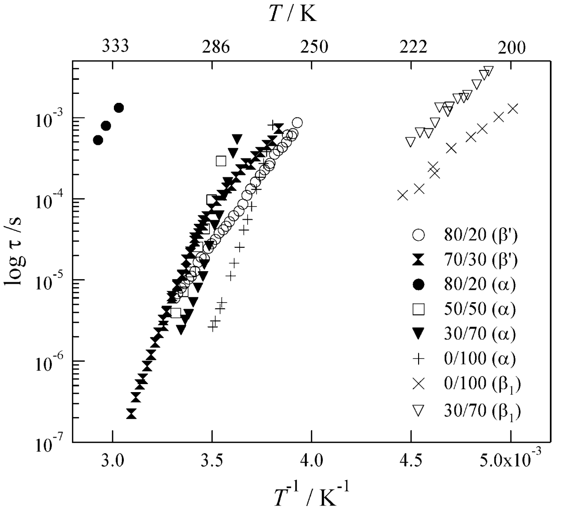

**Figure 5.** Plots of logarithmic relaxation time against reciprocal temperature for α, $\beta_1$, and $\beta'$ processes. The value of $\tau$ in the α process for the 80/20 PS/PVME mixture was obtained from the plot of tan $\delta$ vs temperature.

that the process has a character of orientational motions. The temperature dependence of the relaxation strength for the 70/30 PS/PVME mixture becomes larger at temperature above ca. 290 K (solid line in Figure 4 is a visual guide).

Figure 5 presents a plot of logarithmic relaxation time log $\tau$, which is obtained from $\tau = 1/2\pi f_m$, against reciprocal temperature for various processes.[15] The plot for α processes of neat PVME, 30/70 PS/PVME, and 50/50 PS/PVME mixtures has a curvature (Vogel−Fulcher type) as seen in the usual α process, while it has a linear relation (Arrhenius type) for the $\beta'$ process of the 80/20 PS/PVME mixture. The slope in the Arrhenius plot for the 70/30 PS/PVME mixture changes at $T^{-1} = 0.00345$ K$^{-1}$, below which the slope becomes larger. To make sure whether this change in the slope is valid or not, we investigated the dielectric spectra in the higher frequency range using another dielectric apparatus (HP4184A) and added the result of the relaxation time in Figure 5. The result shows that the temperature dependence of the relaxation time changes with the larger slope in the higher frequency range. At almost the same temperature, we should notice that the temperature dependence of the $\Delta\epsilon$ also becomes larger. We emphasize that the temperature at which the change of the slope takes place is near the glass transition temperature of the mixture. This suggests that the structural relaxation strongly affects the motions. A similar observation has been reported by other researchers.[16] The activation energy $H^*$s evaluated thus are 52 kJ/mol at $0.00345 < T^{-1} < 0.00384$, 125 kJ/mol at $0.00326 < T^{-1} < 0.00345$ for the 70/30 mixture, and 67 kJ/mol for the 80/20 mixture, which are larger than that of the $\beta_2$ process (15−21 kJ/mol) and smaller than that of the α process for neat PVME (167 kJ/mol) or that of the 50/50 PS/PVME mixture (185 kJ/mol) at $f_m = 1.6$ kHz. The $H^*$'s for the $\beta_1$ process of neat PVME and the 30/70 PS/PVME mixture are 39 and 42 kJ/mol, respectively.

Next we show a plot of dielectric loss as a function of logarithmic frequency at a constant temperature for the 80/20 PS/PVME mixture (Figure 6). The large dielectric loss peak had a symmetrical shape and could be fitted with the CC function (eq 1) in the temperature range from 249.4 to 281.3 K. At temperatures higher than 295.8 K, however, the dielectric loss data at low frequencies deviate upward from the CC function. As temperature increases, the magnitude of the deviation from the CC function becomes large and the frequency, at which onset of deviation takes place, shifts toward higher frequency. At 353.6 K, the small broad loss peak can be observed at the low frequencies (see the arrow in Figure 6b). The small broad peak corresponds to the shoulder at about 345 K observed in Figure 1, suggesting the appearance of the α process. The temperature of the small broad peak is slightly higher than the glass-transition temperature $T_g$ obtained by DSC, 339 K. [13] Actually, since in the dielectric measurements we pursue the molecular motions at shorter time scale (at higher frequencies) than at the time scale of DSC measurements, the slight difference is reasonable. The dielectric behavior for the 70/30 PS/PVME mixture is very similar to that for the 80/20 PS/PVME mixture, although we could not clearly observe any clear peak or shoulder for the α process (Figure 7).

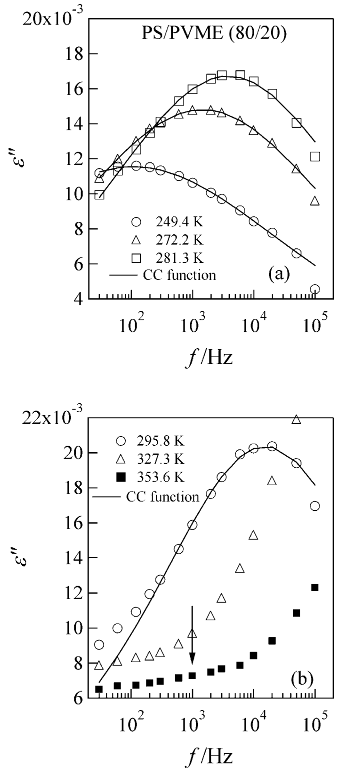

**Figure 6.** Plots of dielectric loss as a function of logarithmic frequency for the 80/20 PS/PVME mixture at various temperatures. The loss data from 249.4 to 281.3 K can be described with the Cole−Cole function (a), while at temperatures higher than 295.8 K, the dielectric loss data at low frequencies deviate upward from the Cole−Cole function (b).

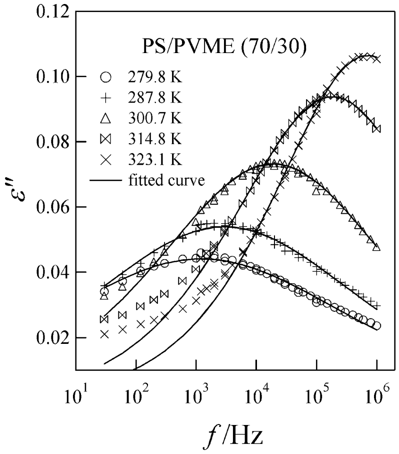

**Figure 7.** Dielectric loss spectra for the 70/30 PS/PVME mixture at various temperatures.

**3.4. Pressure Effects on the Large Loss Peak for the 80/20 Mixture.** Figure 8 shows the temperature dependence of

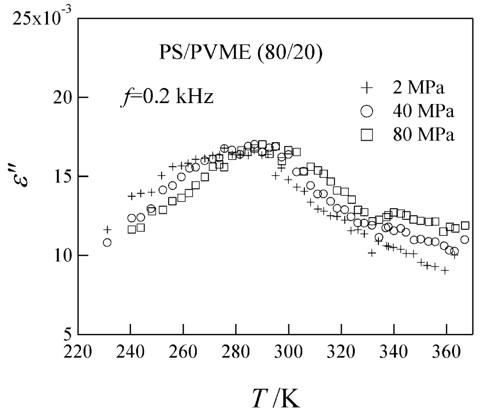

**Figure 8.** Temperature dependence of dielectric loss at $f = 0.2$ kHz for the 80/20 mixture at various pressures.

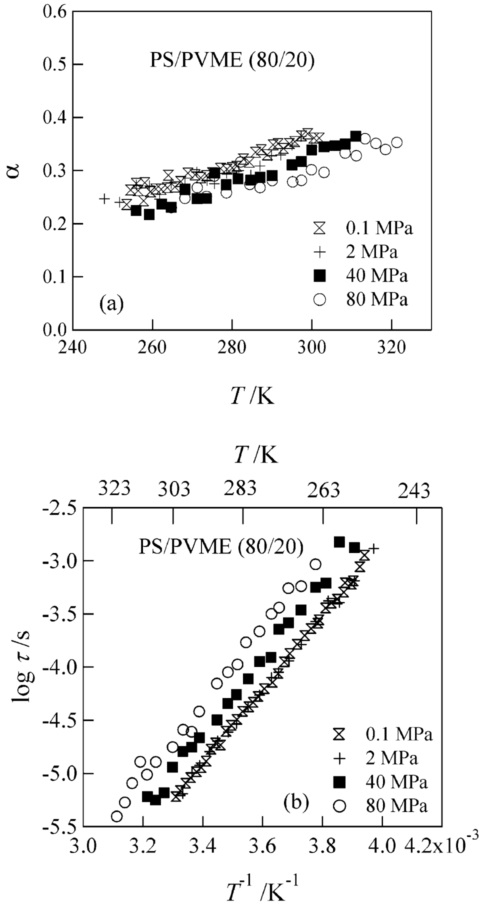

**Figure 9.** (a) Temperature dependence of the parameter α at various pressures. (b) Arrhenius plot at various pressures.

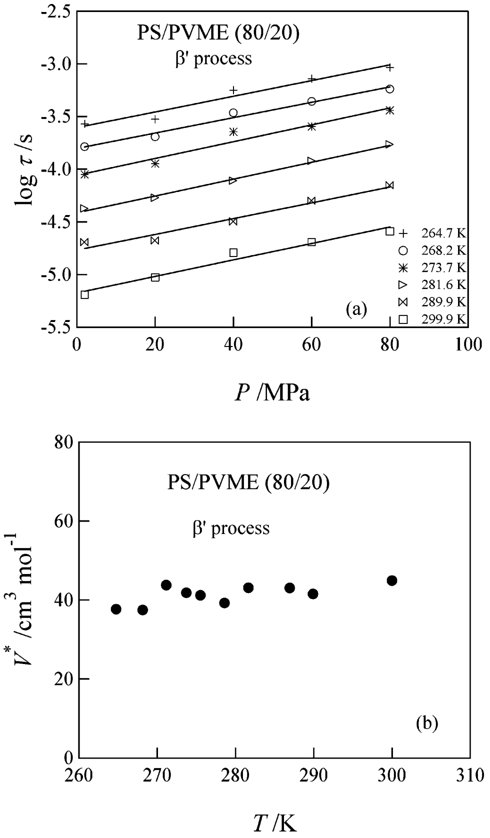

**Figure 10.** Pressure dependence of logarithmic relaxation time at various temperatures for the $\beta'$ process of the 80/20 PS/PVME mixture (a). Temperature dependence of activation volume (b).

dielectric loss at various pressures for the 80/20 PS/PVME mixture. The large loss peak for the $\beta'$ process shifts to higher temperature by applying pressure; i.e., the motions become slow by pressure. The shape of dielectric loss spectra was almost unchanged by pressure, and therefore they were analyzed with eq 1. In Figure 9a, the parameter α at various pressures is plotted against temperature, indicating that α slightly decreases with pressure. Thus, applying pressure leads to a slight change in the distribution of the relaxation time; i.e., the larger the pressure, the slightly broader the distribution. The dielectric relaxation strength hardly changed by pressure in the pressure range covered in our study. In Figure 9b, we show the Arrhenius plot at various pressures. The plot has a linear relation with almost the same slope at all the pressures measured. Thus, although pressure slows down the motion, it hardly affects the activation energy.

We estimated the magnitude of the change in the relaxation time by pressure, i.e., activation volume $V^*$ (Figure 10a).

$$V^* = RT\left[\frac{\partial \ln \tau}{\partial P}\right]_T \tag{4}$$

$V^*$ from the plot in Figure 10a was estimated. The magnitude of $V^*$ is ca. 40 cm$^3$/mol and slightly increases with temperature (Figure 10b). So far, it has been shown for many pure molecular substances that $V^*$ for the α process is larger than that of the local $\beta$ process.[17] The value of $V^*$ estimated here is smaller than the molar volume of monomer unit of PVME, $V_{\mathrm{mon}}$, which is 57.7 cm$^3$/mol at 296 K.[18] It has been shown in many polymers that the ratio of $V^*$ to $V_{\mathrm{mon}}$ is larger than unity in the α process, while it is smaller than unity in the $\beta$ process,[17] although there are exceptions for some polymers. Calculating $V^*$ from data of pressure dependence of the relaxation time of the α process for neat PVME by Alegria et al.,[19] the value of $V^*/V_{\mathrm{mon}}$ is larger than unity, although it strongly depends on temperature, e.g., $V^*$ are 156 and 104 cm$^3$/mol at 270 and 290 K, respectively. Thus, similar to the magnitude of $H^*$, the magnitude of $V^*$ for the $\beta'$ process of the 80/20 PS/PVME mixture is found to be quite smaller than that of the α process for neat PVME.

## 4. Discussion

**4.1. The $\beta_1$ Process.** Concerning the $\beta_1$ process, Urakawa et al. concluded by comparing the temperature dependence of dielectric loss at $f = 1$ kHz of completely dried sample with that of sample treated under humidity that the moisture included in the sample is responsible for this process.[4] (However, even

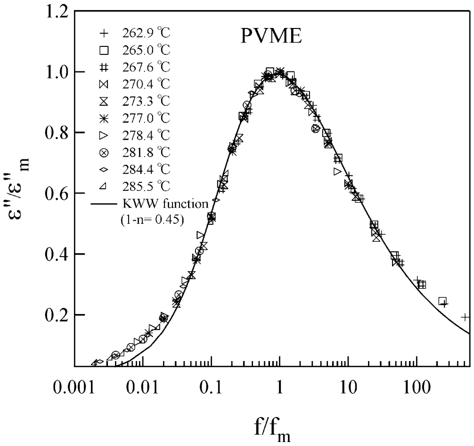

**Figure 11.** Normalized spectrum of the α process for neat PVME. The solid line indicates the transform of the KWW function with $1 - n = 0.45$.

for dried sample the dielectric loss appears to increase broadly in the same temperature region.)

In our experiments, we did our best to remove the effect of moisture in the sample, although it is generally difficult to show that it is completely removable from the sample. From the following analysis, however, there arises another possibility of specifying the process. As is well-known, Johari and Goldstein (JG) showed that there exists a universal $\beta$ process characteristic of amorphous materials irrespective of polymers or small molecules.[20-23] Recently, Ngai et al. suggested that the JG $\beta$ process may play an important role as a precursor to the α process and that it may be related to the primitive relaxation of the coupling model.[24-26] According to the coupling model using the stretch exponent in the Kohlrausch function[27,28]

$$\phi(t) = \exp[-(t/\tau_{\alpha})^{1-n}] \tag{5}$$

the relaxation time $\tau_0$ of the primitive relaxation, which is the precursor to the cooperative α process, is related to the relaxation time $\tau_\alpha$ of the α process as follows:

$$\tau_0 = (t_c)^n (\tau_\alpha)^{1-n} \tag{6}$$

where $t_c$ is the crossover time from independent relaxation to cooperative relaxation and has an approximate value of $2 \times 10^{-12}$ s.[24-26] The relationship between the frequency-dependent dielectric function $\epsilon^*(\omega)$ and $\phi(t)$ is given by the following form:

$$\frac{\epsilon^* - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left(-\frac{\mathrm{d}\phi}{\mathrm{d}t}\right) \exp(-i\omega t)\, \mathrm{d}t \tag{7}$$

Ngai found that $\tau_0$ is approximately equal to the relaxation time of the Johari−Goldstein (JG) $\beta$ process $\tau_{\beta(\mathrm{JG})}$ at $T_g$ in many glass-formers[24]

$$\tau_0(T_g) \approx \tau_{\beta(\mathrm{JG})}(T_g) \tag{8}$$

Here we tested the above relation for the $\beta_1$ process of neat PVME. First, we estimated the stretch exponent $1 - n$ from the fit of eq 7 to the normalized dielectric spectra of the α process as shown in Figure 11 ($1 - n = 0.45$). Second, we evaluated $\tau_0$ from eq 5 using the value of $1 - n = 0.45$ and $\tau_\alpha = 100$ s at $T_g$. The obtained $\log \tau_0(T_g) = -5.5$ is close to the relaxation time of the $\beta_1$ process extrapolated toward $T_g$ in the Arrhenius plot ($\log \tau_{\beta 1}(T_g) = -4.7$). Thus, the $\beta_1$ process can be considered as being related to the JG $\beta$ process. On the other hand, for the 30/70 PS/PVME mixture, a similar analysis turned out to be difficult because the dielectric spectrum for α process could not be well described by the KWW function.

**4.2. The $\beta'$ Process.** Recently, several researchers have discussed dynamic heterogeneity on the grounds that, in the miscible polymer mixtures with a large difference in the glass transition temperature between constituent polymers and without strong intermolecular interactions, two α relaxation processes were observed on the loss spectra.[4,6-8] In the case of our system, the component of PVME is dielectrically active, while that of PS is almost inactive. One may wonder why the large loss peak for the $\beta'$ process of the 80/20 or 70/30 PS/PVME mixture may be due to the α process in the PVME-rich region. However, as shown above, its relaxation behavior is similar to that for a localized molecular motions rather than the α process, such as the Cole−Cole type of the dielectric loss spectra, Arrhenius type of temperature dependence of the relaxation time, and increase of $\Delta\epsilon$ with temperature. Moreover, pressure effects on the relaxation time such as $V^*$ are quite smaller than that of the α process of neat PVME,[19] while it appears to be slightly larger than that of the local process such as side-group motions of many polymers.[17,29] The magnitude of the activation energy $H^*$ estimated for the $\beta'$ process also shows a tendency similar to this. Thus, we see that the large loss peak ($\beta'$ process) for 70/30 and 80/20 PS/PVME mixtures is attributed to molecular motions which are highly restricted in the field frozen below glass transition temperature. Naturally, though the motions can be observed above $T_g$ as well as other local motions, the character of the motions changes because of the change in the surroundings due to the structural relaxation arising from glass transition. As a matter of fact, such a change appears to be observed for the 70/30 PS/PVME mixture. In the above, we showed that the temperature dependence of $\tau$ and $\Delta\epsilon$ change at ca. $T^{-1} \approx 0.00345$ K$^{-1}$or $T = 290$ K. Two factors seem to be considered as causing these behaviors. One is the spectra for the α process overlapping with the spectra of the $\beta'$ process. This will lead to increase in the apparent relaxation strength because we analyzed the spectra with the single CC function. However, this idea cannot explain the change in the slope of the Arrhenius plot, since the appearance of the α process in lower frequencies will apparently shift the peak frequency $f_m$ toward low frequency. Actually, $f_m$ was observed at higher frequency than that expected from the linear behavior of Arrhenius plot; i.e., $\log \tau$ became smaller in comparison with the prediction from the linear behavior. Therefore, we intend to adopt the other viewpoint as follows. Change in the surrounding due to the structural relaxation leads to reorientational motions with larger angles or increase in opportunity of thermal activation process. Here as pointed out by Pathmanathan and Johari et al.,[30] it is important to note that the temperature at which the $\beta'$ process appears is near that of a local $\beta$ process of PS, which may be associated with a conformational change from an out-of-equilibrium conformation to a lower energy conformation.[31] They claimed that the large loss peak for mixture with high concentrations of PS is associated with the local $\beta$ process of PS and an intermolecular cooperativity between PS and PVME exists, although they concluded it only from the temperature dependence of the tan $\delta$ at constant frequency. Their idea does not contradict with our experimental results which are indicative of the character of local motions such as Cole−Cole type of the loss spectra, Arrhenius type of temperature dependence of the relaxation time, or the positive value of $(\partial\Delta\epsilon/\partial T)_p$. Furthermore, this local cooperative motions well explain the moderate magnitude of $H^*$ and $V^*$ and the

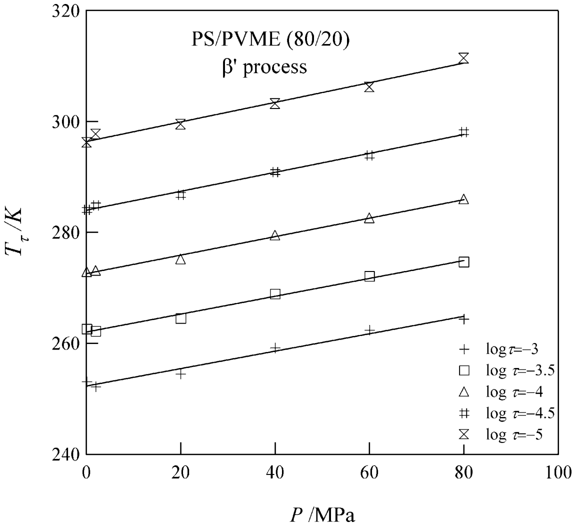

**Figure 12.** Isochronal plot of temperature vs pressure for the $\beta'$ process of the 80/20 PS/PVME mixture.

large dielectric strength. Namely, a change in surroundings through the local motions of PS facilitates the molecular motions of PVME, which leads to a large loss peak. Such local cooperative motions lead to the magnitude of $H^*$ or $V^*$ larger than that of typical local motions. However, since the cooperatively rearranging region is smaller than that of α process, they are smaller than that of α process. The local cooperative motions are different from the α process in the meaning that the former is restricted in the surroundings formed by the structurally frozen field. Thus, though we basically agree with the idea of the local cooperative motions by Pathmanathan and Johari et al., we would like to mention about the statements that in their paper they conclude such local cooperative motions are a proof that there are strong intermolecular interactions between the benzene ring of PS and methyl ether groups of PVME. Our results of pressure experiments appear to preclude the existence of such strong intermolecular interactions. Usually, pressure change in the relaxation time of the substances with strong intermolecular interactions such as hydrogen bonding is smaller in comparison with that of the normal substances with van der Waals type intermolecular interactions. Moreover, to ascertain whether such strong intermolecular interactions exist or not, we obtained temperature change with pressure at constant relaxation time (Figure 12).

$$\left(\frac{\partial T}{\partial P}\right)_\tau = T\frac{V^*}{H^*} \tag{9}$$

As shown in Figure 12, the isochronal plot of temperature vs pressure at various relaxation times is approximately linear in the pressure region covered in our study. The slope is in the range from 0.16 to 0.18 K/MPa, which is close to the pressure coefficient of $T_g$ for neat PVME.[10] We should notice that it is near the value of normal molecular substances rather than that of substances with strong intermolecular interactions; i.e., this mixture is suggested to be a van der Waals type mixture. For substances with strong intermolecular interactions, the value should be smaller.[32] It is likely that after the conformational change of PS with bulky benzene groups the molecular motions of PVME with small side groups are facilitated, even if there are no strong intermolecular interactions.

The ratio of activation energy at constant volume $H_V^*$ to that at constant pressure $H_p^*$ is a useful measure to quantify the relative effect of thermal energy and volume on temperature dependence of relaxation time[10,33]

$$\frac{H_V^*}{H_p^*} = 1 - \gamma\left(\frac{\partial T}{\partial P}\right)_\tau \tag{10}$$

with

$$H_V^* = R\left(\frac{\partial \ln \tau}{\partial(1/T)}\right)_V \tag{11}$$

and

$$H_p^* = R\left(\frac{\partial \ln \tau}{\partial(1/T)}\right)_p \tag{12}$$

where $\gamma$ is the thermal pressure coefficient expressed in the following form:

$$\gamma = \left(\frac{\partial P}{\partial T}\right)_V \tag{13}$$

When the ratio is close to unity, the dynamics is dominated by temperature, while when this value is close to zero, it is dominated by volume. Many van der Waals type liquids including small molecules or polymers have the ratio $H_V^*/H_p^*$ lying from 0.5 to 0.8.[10,11]

Using the PVT data in the literature for the 80/20 PS/PVME mixture,[34] we calculated the above value, which leads to $H_V^*/H_p^* = 0.74$ and 0.75 at 253 and 284 K, respectively. This value is slightly larger than that of the α processes of neat PVME or PS/PVME mixtures with low concentration of PS[11] and is smaller than that of the usual $\beta$ process.[35] This result indicates that the volume effect on the relaxation process is slightly smaller than that of the α process of neat PVME or PS/PVME mixtures with low concentration of PS, while it is larger than the usual $\beta$ process. This may reflect the fact that the $\beta'$ process has somewhat cooperative character, although the cooperative region is smaller than that of the usual α process.

Finally, we show that the temperature of $\beta'$ process extrapolated from Arrhenius plot toward the time scale of glass transition temperature (ca. 100 s) is not quite consistent with the calorimetric $T_g$ for mixtures with high PS concentration. As mentioned above, the relaxation time for α processes of neat PVME and 30/70 and 50/50 mixtures shows non-Arrhenius behavior (see Figure 5), such as the Vogel−Fulcher type of temperature dependence:

$$\log \tau = \log \tau_0 + B/(T - T_\infty) \tag{14}$$

with empirical constants $\tau_0$, $B$, and $T_\infty$. We extrapolated the curve fitted with eq 14 to $\log \tau = 2$ and obtained the temperature at $\log \tau = 2$, which is consistent with the glass transition temperature obtained by DSC measurements of Bank et al.,[13] as shown in Figure 13. The composition dependence of $T_g$ for this system is always far below that expected by the Flory−Fox relation, which is based upon iso-free volume at $T_g$:

$$1/T_{g,m} = \phi_A/T_{g,A} + \phi_B/T_{g,B} \tag{15}$$

where $T_{g,m}$ and $T_{g,i}$ are the glass transition temperatures for mixture and component $i$ ($i$ = A or B), respectively. This result also may imply the lack of the strong intermolecular interactions between PS and PVME because this kind of interaction should decrease flexibilities of backbone chains and therefore should increase the glass transition temperature $T_g$. On the other hand, in a similar manner for each of the $\beta'$ processes of 70/30 and

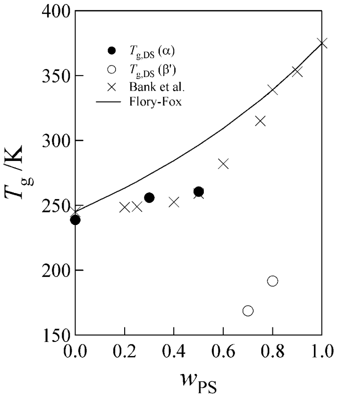

**Figure 13.** Comparison between $T_g$ obtained by DSC[13] and the temperatures at log $\tau = 2$ estimated from the Vogel−Fulcher equation in the α process and from the Arrhenius equation in the $\beta'$ processes of 70/30 and 80/20 PS/PVME mixtures.

80/20 PS/PVME mixtures, we obtained the temperature at log $\tau = 2$ and also added it in Figure 13. Both of the temperatures obtained thus for the $\beta'$ process are much lower than the glass transition temperature of the mixture. We believe that if the $\beta'$ peak is attributed to the α relaxation of the PVME-rich region with lower $T_g$, at least in the long time limit or in the small frequency (strictly in the limit of zero frequency), it should approach the other α relaxation of the PS-rich region with high $T_g$, as long as the mixture is miscible in the segmental scale.[36] However, the above results do not show such behavior. Thus, we can conclude that the large loss peak of 70/30 and 80/20 PS/PVME mixtures is not due to the α process.

## 5. Conclusion

The molecular motions for PS/PVME mixtures were investigated by use of dielectric spectroscopy as functions of temperature and pressure. Both temperature and pressure dependence of the dielectric behaviors indicate that the largest dielectric loss peak for mixtures with high PS concentrations is attributed to cooperative local motions constrained to the surroundings formed by the PS matrix.

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