

## Miscibility and Molecular Motion of Poly(methyl acrylate)/Poly(vinyl acetate) Blend as Studied by $^{13}\text{C}$ NMR in the Solid State

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**ABSTRACT:** Miscibility and molecular motion of a poly(methyl acrylate)/poly(vinyl acetate) blend are studied by high-resolution solid-state  $^{13}\text{C}$  NMR techniques. Observed  $^1\text{H}$  relaxation times indicate that they are miscible on the scale of 20–30 Å. The temperature dependence of the  $^{13}\text{C}$  linewidth is examined to investigate effects of blending on molecular motion of each component polymer. Two models for the temperature dependence of the correlation time of motion are examined. One is an Arrhenius dependence and the other is a WLF dependence. Both models explain the observed temperature dependence adequately. It is shown that by blending molecular motions of PMA and PVAc becomes similar.

**KEY WORDS** Miscibility / Molecular Motion / Polymer Blend / Poly(methyl acrylate) / Poly(vinyl acetate) / High-Resolution  $^{13}\text{C}$  Solid-State NMR /

For most polymer pairs to be miscible, a certain exothermic interaction is required to overcome the disadvantage of free volume difference between the component polymers. To phrase differently, if they have similar  $P-V-T$  properties, they are likely to be miscible without a specific interaction. Nandi *et al.* studied miscibility of poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) by the inverse gas chromatography method in several solvents.<sup>1</sup> They concluded that the PMA/PVAc blend is miscible, and no specific interactions are operative.  $^1\text{H}$  NOE experiments on the PMA/PVAc blend in acetone also showed that they are well mixed on a molecular level in acetone solution.<sup>2</sup> To explain the observed intimacy between the side-chain  $\text{OCH}_3$  group of PMA and the main-chain CH proton of PVAc, an inter-polymer hydrogen bonding was invoked. Further, it was found that the  $^{13}\text{C}$  spin-lattice relaxation times are affected by

blending. This shows that the molecular motions of both PMA and PVAc are affected by blending. Even though they have very similar  $P-V-T$  properties, there is still appreciable free volume difference. In this work, we examine miscibility and molecular motion of PMA/PVAc blends in the solid state by using high-resolution  $^{13}\text{C}$  solid-state NMR methods.

### EXPERIMENTAL

Poly(methyl acrylate) (PMA) and poly(vinyl acetate) (PVAc) were purchased from Aldrich Chemical Company, Inc. The weight average molecular weight is 30700 for PMA and 124800 for PVAc. PMA was dried in vacuum at 90°C for 7 days. PMA and PVAc were dissolved in acetone respectively at a concentration of  $\sim 5\text{wt}/\text{v}\%$  and mixed for a day in compositions of PMA:PVAc = 25:75, 50:50, and 75:25 in

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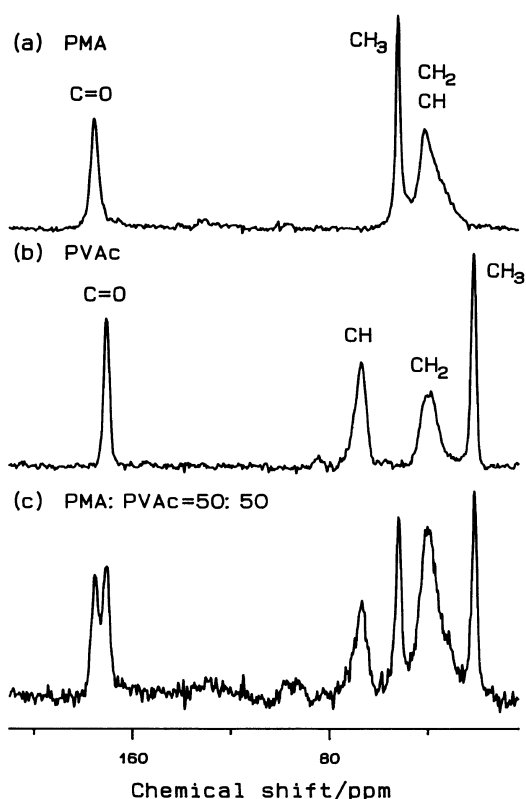
a monomer-units ratio. Blend samples were obtained by casting the solution on a glass plate and dried under vacuum at  $90^\circ\text{C}$  for a week.

Differential scanning calorimetry (DSC) measurements were done on a Mettler DSC20 with a heating rate of  $10\text{ K min}^{-1}$ .

NMR experiments were carried out on a JEOL JNM-GX270 spectrometer operating at resonance frequency of  $67.8\text{ MHz}$  for  $^{13}\text{C}$ . High-resolution  $^{13}\text{C}$  NMR was realized by magic-angle sample spinning (MAS) and high-power proton spin decoupling (DD). The radio-frequency (rf) field strength was about  $55.6\text{ kHz}$ . To enhance the signal-to-noise ratio, the cross-polarization (CP) technique was applied to the measurements below room temperature ( $300\text{ K}$ ). Since the CP efficiency is low above room temperature, the conventional  $90^\circ$  pulse method was employed. The  $^{13}\text{C}$  chemical shifts were calibrated in ppm relative to TMS by taking the methine carbon nuclei of solid adamantane ( $29.5\text{ ppm}$ ) as an external reference standard. Variable-temperature measurements were made using a JEOL MVT temperature controller. Temperature calibration was done by the conventional methanol method. The proton spin-lattice relaxation time,  $T_1$ , and the proton spin-lattice relaxation time in the rotating frame,  $T_{1\rho}$ , were measured at room temperature by the inversion recovery method and the conventional spin-lock method, respectively.

## RESULTS AND DISCUSSION

Our previous  $^1\text{H}$  NOE experiments showed that the inter-proton distance between the  $\text{OCH}_3$  group of PMA and the main-chain CH of PVAc is  $3.4\text{ \AA}$  in acetone.<sup>1</sup> This intimacy led us to invoke a weak inter-polymer hydrogen bonding. In acetone, no appreciable spectral changes occur on mixing. In solids, since effects of a hydrogen bonding interaction are not weakened by molecular overall motion, we expected to observe the effects on spectra. The CP/MAS  $^{13}\text{C}$  NMR spectra of PMA, PVAc,



**Figure 1.**  $^{13}\text{C}$  DD/MAS NMR spectra of (a) PMA, (b) PVAc, and (c) the PMA:PVAc=50:50 blend at room temperature.

and the 50:50 blend are shown in Figure 1. No appreciable shifts due to blending were observed for the temperatures we studied, showing that the inter-polymer hydrogen bonding interaction is weak in solids.

### Miscibility

A single glass-transition temperature  $T_g$  was observed for the 50:50 blend at  $295\text{ K}$ , which is in good agreement with an average of those observed for the pure polymers ( $T_g$  of PMA is  $283\text{ K}$  and that of PVAc is  $305\text{ K}$ ). This shows thermodynamical miscibility of the blend.<sup>1</sup>

To investigate miscibility on smaller spatial scales, the spin-lattice relaxation time of  $^1\text{H}$  in the laboratory frame ( $T_1$ ) and that in the rotating frame ( $T_{1\rho}$ ) were observed for component polymers through well-resolved  $^{13}\text{C}$

**Table I.** Observed and calculated  $^1\text{H}$   $T_1$  values (s) of PMA/PVAc blends<sup>a</sup>

		Pure	Blend (PMA : PVAc)		
			25 : 75	50 : 50	75 : 25
PMA	CH <sub>3</sub>	2.50 ± 0.02	3.3 ± 0.4	3.08 ± 0.04	2.83 ± 0.03
	C=O	2.65 ± 0.08	3.6 ± 0.3	3.1 ± 0.1	2.89 ± 0.06
PVAc	CH <sub>3</sub>	3.24 ± 0.07	3.26 ± 0.08	3.34 ± 0.04	3.05 ± 0.05
	CH	3.00 ± 0.07	3.18 ± 0.08	3.03 ± 0.05	2.7 ± 0.2
	C=O	3.2 ± 0.2	2.8 ± 0.1	3.1 ± 0.1	3.00 ± 0.07
Calcd <sup>b</sup>			3.0	2.8	2.7

<sup>a</sup> Error is 2.5 $\sigma$ . <sup>b</sup> Calculated from eq 2.

**Table II.** Observed and calculated  $^1\text{H}$   $T_{1\rho}$  values (ms) of PMA/PVAc blends<sup>a</sup>

		Pure	Blend (PMA : PVAc)		
			25 : 75	50 : 50	75 : 25
PMA	CH <sub>3</sub>	2.49 ± 0.02	10 ± 2	9.0 ± 0.4	4.52 ± 0.09
	C=O	2.8 ± 0.3	9 ± 1	9.6 ± 0.5	5.1 ± 0.1
PVAc	CH <sub>3</sub>	31 ± 1	8.3 ± 0.6	10.7 ± 0.3	5.6 ± 0.2
	CH	34 ± 4	10.5 ± 0.7	13.1 ± 0.7	7.0 ± 0.5
	C=O	28 ± 3	9.2 ± 0.7	11.9 ± 0.9	6.4 ± 0.3
Calcd <sup>b</sup>			8.4	4.9	3.4

<sup>a</sup> Error is 2.5 $\sigma$ . <sup>b</sup> Calculated from eq 2.

signals. A single exponential decay was observed for all relaxation experiments performed. Tables I and II list the observed  $T_1$  and  $T_{1\rho}$ , respectively, of pure PMA, pure PVAc, and those in the blends. For all blends examined, the observed relaxation times of PMA and PVAc are essentially identical, indicating a fast spin diffusion between PMA and PVAc. A maximum diffusive path length  $L$  may be derived as:<sup>3,4</sup>

$$L = (6Dt)^{1/2} \quad (1)$$

By assuming a spin diffusion coefficient  $D$  of  $\sim 10^{-12} \text{ cm}^2 \text{ s}^{-5}$  and  $t = 10 \text{ ms}$  for  $T_{1\rho}$  experiments,  $L = 20 \sim 30 \text{ \AA}$  is deduced. Therefore, if heterogeneity is present in the blends, their linear dimensions are less than  $20 \sim 30 \text{ \AA}$ . We thus conclude that the two polymers are microscopically miscible for all compositions

examined.

If the blending does not alter molecular motion of each component polymer and the  $^1\text{H}$  spin diffusion is fast, the  $^1\text{H}$  relaxation rate of a blend,  $(T_1^{\text{Blend}})^{-1}$ , is given as an average of those of component polymers,  $(T_1^{\text{PMA}})^{-1}$  and  $(T_1^{\text{PVAc}})^{-1}$ , weighted by the ratio of the proton number,  $f_{\text{PMA}}$  and  $f_{\text{PVAc}}$  ( $f_{\text{PMA}} + f_{\text{PVAc}} = 1$ ) as<sup>3,6</sup>:

$$(T_1^{\text{Blend}})^{-1} = f_{\text{PMA}}(T_1^{\text{PMA}})^{-1} + f_{\text{PVAc}}(T_1^{\text{PVAc}})^{-1} \quad (2)$$

Similar equation can be written for  $T_{1\rho}$ . Since it is difficult to observe the intrinsic relaxation time of the component polymer in the blend, we adopted the observed relaxation times of pure PMA and pure PVAc in the calculation. The calculated relaxation rates by using eq 2 are also collated in Tables I and II. The calculated  $T_1$  values are in good agreement with the observed values, while the calculated

$T_{1\rho}$  values for the 50:50 and 75:25 blends deviate from the corresponding experimental values. This disagreement is attributed to the use of the observed relaxation times of pure polymers in eq 2. It is envisaged that molecular motions of the component polymers are affected by blending. Especially, motions of a few 10 kHz are affected, because  $T_{1\rho}$  is sensitive to molecular motion of a few 10 kHz. To investigate effects of blending on motion, we observed temperature dependence of <sup>13</sup>C signals, because the <sup>13</sup>C linewidth under DD/MAS is also very sensitive to motion of a few 10 kHz.<sup>7,8</sup>

### Molecular Motion

Figures 2–4 show <sup>13</sup>C spectra of pure PMA (Figure 2), pure PVAc (Figure 3), and the 50:50 blend (Figure 4) at various temperatures.

At temperatures below  $T_g$ , they are independent of temperature. As the temperature increases above  $T_g$ , the lines broaden and reach to maximum broadening at around 330 K. Further heating brings line narrowing. This behavior can be explained by the onset of an overall chain motion at the glass-transition temperature.<sup>7</sup> Indeed, the temperature dependence of the linewidth of each carbon site is quite similar. This means that the motion affecting the linewidth is an overall motion of a polymer chain. Since it is difficult to separate the CH and CH<sub>2</sub> signals of PMA, we compare the linewidths of the C=O carbons of PMA and PVAc. In the blend, the linewidths of the overlapped C=O carbons were separated by fitting the signal to a sum of two Lorentz lines. Figures 5 and 6 show the temperature dependence of the linewidth of the C=O

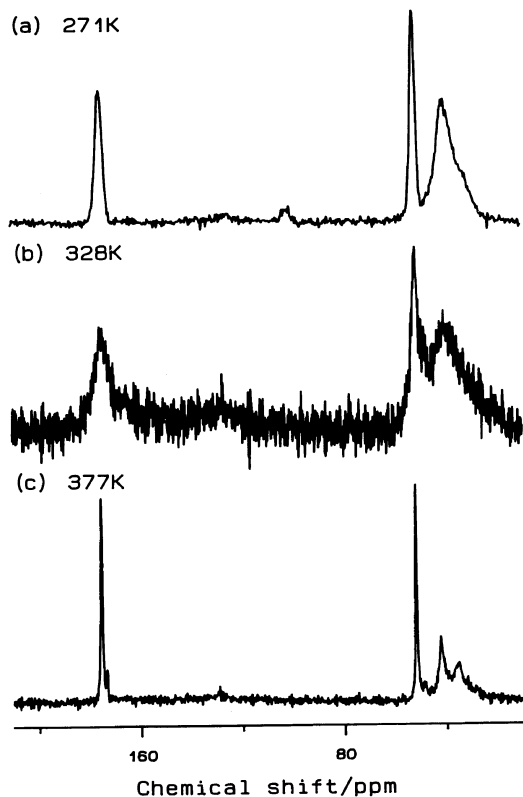


Figure 2. <sup>13</sup>C MAS NMR spectra of PMA at (a) 271 K, (b) 328 K, and (c) 377 K.

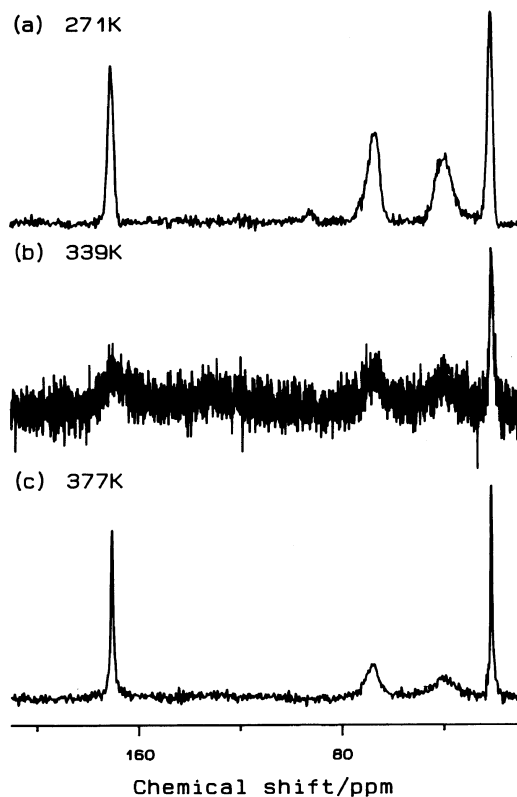


Figure 3. <sup>13</sup>C MAS NMR spectra of PVAc at (a) 271 K, (b) 339 K, and (c) 377 K.

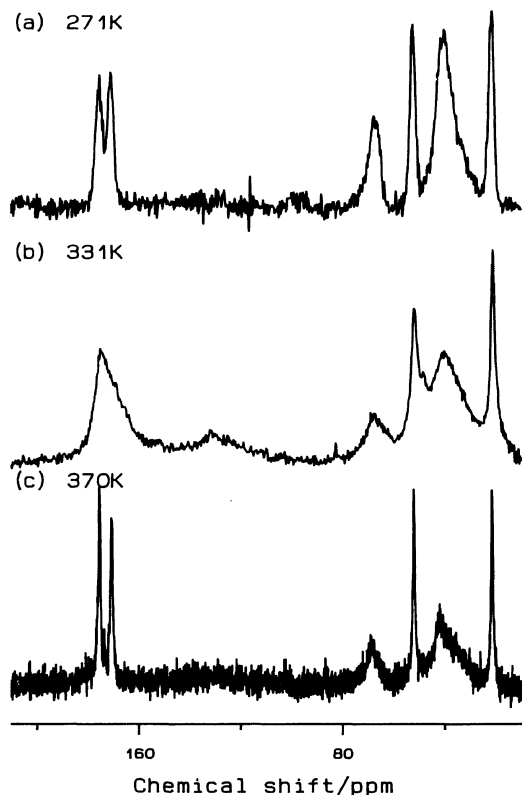


Figure 4.  $^{13}\text{C}$  MAS NMR spectra of the PMA:PVAc = 50 blend at (a) 271 K, (b) 331 K, and (c) 370 K.

carbon in pure polymers (Figure 5) and in the 50:50 blend (Figure 6) (PMA (O) and PVAc ( $\times$ )).

The observed full linewidth ( $\delta$ ) at half height of the C=O signal may be written as a function of temperature  $T$  as<sup>7</sup>:

$$\delta = \delta_0 + \delta_1(2/\pi)\arctan(\alpha(T_0 - T)) + A\tau(1 + \omega_1^2\tau^2) \quad (3)$$

Here,  $\delta_0$  represents the intrinsic linewidth accounting for various static line-broadening mechanisms, such as inhomogeneous static field and misalignment of the magic angle. The second term represents motional narrowing of a distribution of the isotropic chemical shift arising from a variety of local conformations of polymer in the glassy state. It is assumed to have an arctangent dependence on temperature.  $\delta_1$  is the half of the linewidth due to the

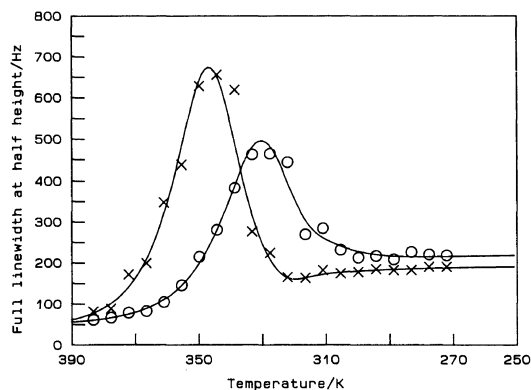


Figure 5. Temperature dependence of the linewidth of the C=O carbon of pure PMA (O) and pure PVAc ( $\times$ ) as a function of temperature. The solid curves are "best fit" ones described in the text.

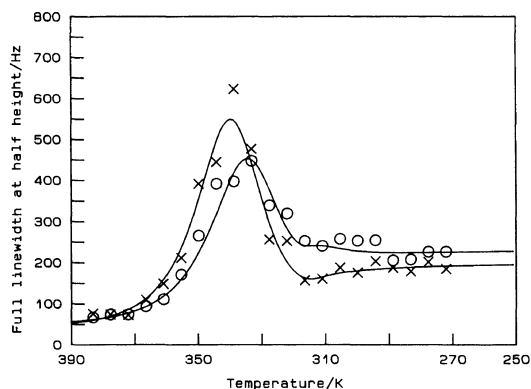


Figure 6. Temperature dependence of the linewidth of the C=O carbon of PMA (O) and PVAc ( $\times$ ) in the PMA:PVAc = 50:50 blend as a function of temperature. The solid curves are "best fit" ones described in the text.

distribution of the isotropic chemical shift.  $\alpha$  and  $T_0$  represent the steepness and the characteristic transition temperature of this narrowing, respectively. The third term is the linewidth due to the C-H dipolar interaction reintroduced by an interference of the applied proton decoupling and molecular motion.<sup>8</sup> This term makes a maximum contribution of  $A/(2\omega_1)$  when  $\omega_1\tau = 1$ , where  $\tau$  is the correlation time of molecular motion and  $\omega_1$  is the decoupling strength.  $A$  denotes the reduction of the  $^{13}\text{C}$ - $^1\text{H}$  second moment due to molecular motion and can be written as;

**Table III.** Best fit parameters to the linewidth data of the C=O carbon using the Arrhenius equation<sup>a</sup>

	$E_a/\text{kcal mol}^{-1}$	$\tau_0 \times 10^{21}/\text{s}$	$A \times 10^{-6}/\text{s}^{-2}$	$\delta_0/\text{Hz}$	$\delta_1/\text{Hz}$	$\alpha$	$T_0/\text{K}$
Pure PMA	21 ± 1	40 ± 80	3.0 ± 2	135 ± 5	91 ± 8	0.13 ± 0.07	313 ± 5
Blend PMA	23 ± 2	5 ± 20	2.7 ± 2	140 ± 8	93 ± 11	0.2 ± 0.2	316 ± 4
Blend PVAc	25 ± 3	0.2 ± 0.7	3.5 ± 3	121 ± 9	81 ± 13	0.1 ± 0.1	313 ± 3
Pure PVAc	26 ± 2	0.2 ± 0.5	4.4 ± 3	117 ± 9	80 ± 11	0.13 ± 0.08	319 ± 3

<sup>a</sup> Error is 2.5σ.

$$A = \lambda M_2 \quad (4)$$

$M_2$  is the powder average of the second moment of the static <sup>13</sup>C-<sup>1</sup>H dipolar interaction.  $\lambda$  is the reduction factor of the second moment ( $0 < \lambda < 1$ ) due to motion. When the motion is isotropic,  $\lambda = 1$ .

The temperature at the maximum broadening  $T_{\text{max}}$  is about 330 K for pure PMA and about 350 K for pure PVAc, while those in the blend are about 340 K for both PMA and PVAc. The difference of  $T_{\text{max}}$  between PMA and PVAc in the blend is obviously smaller than that for component polymers. This shows that both polymers have similar correlation times at around 340 K in the blend, and is consistent with the observed averaging of  $T_g$  by blending.

There exist two possible expressions for temperature dependence of the correlation time  $\tau$ . One is the Arrhenius equation and the other is the Williams, Landel, and Ferry (WLF) equation.<sup>9</sup> Firstly, we adopt an Arrhenius dependence on temperature as;

$$\tau = \tau_0 \exp(E_a/RT) \quad (5)$$

where  $E_a$  is the activation energy and  $\tau_0$  is the correlation time at infinite temperature. The observed linewidths were fitted to eq 3 and 5 by taking  $\delta_0$ ,  $\delta_1$ ,  $\alpha$ ,  $T_0$ ,  $A$ ,  $\tau_0$ , and  $E_a$  as fitting parameters. The least-squares fitted parameters are listed in Table III, and the solid lines in Figures 5 and 6 are the "best fit" lines.

The difference of the activation energy  $E_a$  for pure polymers is 5 kcal mol<sup>-1</sup>. While in the blend, the difference becomes 2 kcal mol<sup>-1</sup>.

Further, the characteristic temperature  $T_0$  of PVAc decreases from 319 K to 313 K by blending. While  $T_0$  of PMA increases from 313 K to 316 K. The motional behavior of each component polymer becomes similar in the blend.

From the present experiments, it is difficult to obtain a concrete model for a polymer motion. The  $A$  value (*i.e.*, the maximum linewidth) for PVAc in the blend is slightly smaller than that for pure PVAc. Similarly, the  $A$  value of PMA decreases in the blend. The reduction of  $A$  can be attributed to increase of the motional anisotropy in the blend. Similar reduction of the maximum linewidth in a blend has also been found for polystyrene/poly(vinyl methyl ether)<sup>7</sup> and poly(ethylene oxide)/poly(vinylphenol).<sup>11</sup> The  $\tau_0$  values are  $\sim 10^{-7}$  times smaller than those obtained for a simple motion such as rotation of a methyl group. The small  $\tau_0$  value may indicate that the motion is correlated<sup>10</sup> and can not be expressed by a single correlation time.

From the correlation time we deduced, it is possible to calculate the intrinsic relaxation time of the component polymer. By adopting the calculated intrinsic relaxation times to eq 2, one should be able to observe a better agreement with the observed relaxation time. However, since the motional model of the component polymer is still unclear, we have not tried to calculate <sup>1</sup>H relaxation times.

Secondly, we employ the WLF equation to express the correlation time  $\tau$  as<sup>9</sup>:

$$\log(\tau/\tau_s) = C_1(T - T_s)/(C_2 + T - T_s) \quad (6)$$

**Table IV.** Best fit parameters to the linewidth data of the C=O carbon using the WLF equation<sup>a,b</sup>

	$\tau_s/s$	$T_s/K$
Pure PMA	$(12 \pm 6) \times 10^{-4}$	$287 \pm 5$
Blend PMA	$(10 \pm 9) \times 10^{-4}$	$294 \pm 10$
Blend PVAc	$(3 \pm 4) \times 10^{-4}$	$307 \pm 9$
Pure PVAc	$(6 \pm 5) \times 10^{-4}$	$310 \pm 8$

<sup>a</sup> Error is  $2.5\sigma$ . <sup>b</sup> Other five parameters are omitted.

where  $\tau_s$  is the correlation time at a reference temperature  $T_s$ .  $C_1$  and  $C_2$  are the "universal" constants of the WLF equation. We choose to use  $-8.86$  and  $101.6/\text{deg}$  for  $C_1$  and  $C_2$ , respectively. The observed linewidths were fitted to eq 3 and 6 by taking  $\delta_0$ ,  $\delta_1$ ,  $\alpha$ ,  $T_0$ ,  $A$ ,  $\tau_s$ , and  $T_s$  as adjustable parameters. It is worth to note that the number of the adjustable parameters is same as that used when the Arrhenius equation is adopted. The "best fit" parameters are listed in Table IV. Since the "best fit" values for  $\delta_0$ ,  $\delta_1$ ,  $\alpha$ ,  $T_0$ , and  $A$  are agreed with those listed in Table III within error, we have not listed them in Table IV. Also the calculated lines are almost identical to those in Figures 5 and 6, we have not shown them in the Figures.

Since we chose  $C_1 = -8.86$  and  $C_2 = 101.6$ , we naively expected to find the "universal" relation of  $T_s \sim T_g + 50 \text{ K}$ .<sup>9</sup> However, the "best fit" values for pure polymers and those in the blend are 5 K higher than the corresponding  $T_g$  values. Therefore, it is invoked that the "universal" relation in the present case is written as  $T_s \sim T_g + 5 \text{ K}$ . In fact, we have reexamined the linewidth data of poly(methyl vinyl ether) (PVME)<sup>7</sup> to find that its temperature dependence can also be reproduced by using the WLF equation with  $T_s = T_g + 5 \text{ K}$ ,  $C_1 = -8.86$ , and  $C_2 = 101.6$ .

The reference temperature for the  $^{13}\text{C}$  linewidth is 45 K lower than those observed for the rheological properties. This may be understood as follows. The lower reference

temperature indicates that the motion detected by the  $^{13}\text{C}$  linewidth measurement enjoys a larger free volume to move as compared to those detected by the rheological methods. The temperature dependence of the  $^{13}\text{C}$  linewidth is governed by the local fluctuation of the CH dipolar interaction. While the rheological methods observe macroscopic properties, which are mainly governed by an overall polymer motion. Since the space requirement for the local fluctuation of the CH group is less than that for the overall motion, the former appears to have a larger free volume, leading to a lower reference temperature. Currently we are investigating whether this set of the WLF coefficients is applicable to other polymers. The results and more detailed discussion will be published elsewhere.

For polymers in a blend, the existence of a set of "universal" coefficients of the WLF equation for polystyrene (PS) in PS/PVME has also been suggested by Menestrel *et al.*<sup>12</sup> In fact, our PMA/PVAc results indicate that the abovementioned set of the coefficients can be applied to polymers in a blend. It is difficult, however, to verify this experimentally. Since even though the blend shows an apparent single glass transition, its component polymers may have different correlation times.<sup>7,11-13</sup> We must observe the glass transition temperature of each component polymer separately in a blend, if we are to establish the "universal" relation for a blend system.

To conclude, the relaxation times measurements show that PMA and PVAc are miscible on the scale of 20–30 Å. In comparing the calculated relaxation times and the observed ones, we realized that motion of each component polymer in the blend is different from that of pure polymer. Effects of blending on motion of component polymers are studied by observing the temperature dependence of the  $^{13}\text{C}$  linewidths. The observed temperature dependence is analyzed qualitatively by employing either the Arrhenius equation or the WLF equation for a correlation time. The

activation energies for the component polymers in the blend become similar by blending. The analyses using the WLF equation show that the reference temperatures of the component polymer in the blend becomes similar by blending. These averaging phenomena of the motional parameters of component polymers have been found for other polymer blends.<sup>7,11-13</sup> In PMA/PVPh, the averaging is much effective as compared to others. Since both polymers have similar  $P-V-T$  properties, the molecular environments of PMA and PVAc are facile to be averaged by blending.

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