Poly(vinylphenol)/Poly(methyl acrylate) and Poly(vinylphenol)/Poly(methyl methacrylate) Blends: Hydrogen Bonding, Miscibility, and Blending Effects on Molecular Motions As Studied by ^{13}C CP/MAS NMR

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ABSTRACT: A variety of NMR parameters including ^{13}C chemical shifts, ^{13}C linewidth (T_2), ^{13}C $T_{1\rho}$, ^{1}H $T_{1\rho}$, and ^{1}H T_1 have been measured in the solid state to examine the intermolecular interaction, miscibility, and molecular motion of poly(4-vinylphenol)/poly(methyl acrylate) (PVPh/PMA) and poly(4-vinylphenol)/poly(methyl methacrylate) (PVPh/PMMA) blends. Observed downfield shifts of ^{13}C resonances of the carbonyl carbon of PMA and the phenolic hydroxyl carbon of PVPh in PVPh/PMA blends are ascribed to intermolecular hydrogen-bonding interaction between two different polymers. Such downfield shifts are not appreciable for PVPh/PMMA blends. The results of ^{1}H T_1 and ^{1}H $T_{1\rho}$ indicate that the PVPh/PMA blends are intimately mixed on a scale of 20–30 Å at all compositions. On the other hand, the miscibility of PVPh/PMMA blends is poor; the domain size is larger than 200–300 Å. The α-methyl group of PMMA brings about quite different miscibility. Furthermore, ^{1}H $T_{1\rho}$, ^{13}C $T_{1\rho}$, and the temperature dependence of the ^{13}C linewidth (T_2) provide clear evidence that the motional state of PMA is greatly affected by blending with PVPh at lower temperatures. At higher temperatures the blending effect on molecular motion is observable for both components. Such blending effects also show composition dependence.

Introduction

In previous papers,[1-4] we presented the results of NMR studies on a number of binary miscible polymer systems containing poly(vinyl alcohol), in which the hydrogen bonding is the dominant intermolecular interaction. As with poly(vinyl alcohol), poly(4-vinylphenol) (PVPh) has a hydroxyl group in the aromatic ring that can act as a hydrogen-bonding donor. PVPh possibly associates with a polymer having a hydrogen-bonding acceptor to form a miscible blend.

Coleman and co-workers reported a series of Fourier transform infrared spectroscopy (FT-IR) studies on PVPh blends with poly(vinyl acetate), ethylene–vinyl acetate copolymers,[5] polyesters, poly(vinyl alkyl ethers), poly(ethylene oxide), and poly(vinylpyrrolidone).[6] They showed that the phenolic hydroxyl group of PVPh can form intermolecular hydrogen bonds with several kinds of hydrogen-bonding acceptors. Phase diagrams were estimated theoretically for a number of PVPh blends and compared with experimental observations.[7] For PVPh/polyacrylate blends[7] the phase diagrams deduced from theoretical and experimental studies indicated that PVPh/poly(methyl acrylate) and PVPh/(ethyl acrylate) blends are miscible over a wide temperature range. PVPh/poly(butyl acrylate) and PVPh/poly(pentyl acrylate) systems were found to show phase separation.

In this work, ^{13}C cross polarization/magic angle sample spinning (CP/MAS) NMR spectra of poly(4-vinylphenol)/poly(methyl acrylate) (PVPh/PMA) and poly(4-vinylphenol)/poly(methyl methacrylate) (PVPh/PMMA) blends have been observed in order to study intermolecular hydrogen bonding. The miscibility and microphase structure of these blends on scales from 20–30 to 200–300 Å have been investigated by measuring the ^{1}H spin–lattice relaxation times in both the rotating frame ($T_{1\rho}$) and the laboratory frame (T_1) through well-resolved ^{13}C resonances. The temperature dependences of ^{13}C T_2 (line width), ^{13}C $T_{1\rho}$, and ^{1}H $T_{1\rho}$ are discussed in terms of blending effects on the molecular motion and the domain structure. The results of PVPh/PMMA are compared with those of PVPh/PMA in order to examine the effect of the α-methyl group on the miscibility.

Experimental Section

Samples. PVPh was obtained from Polysciences Inc. The molecular weight is 1500–7000. PMA and PMMA were obtained from Aldrich Chemical Co., Inc. Number- and weight-average molecular weights, M_n and M_w, of PMA are 10 600 and 30 700, respectively. M_n and M_w of PMMA are 46 400 and 93 300, respectively. Glass transition temperatures of PVPh, PMA, and PMMA are 393, 283, and 378 K, respectively.

PVPh/PMA and PVPh/PMMA blends were preparerd by the solution-cast method using tetrahydrofuran (THF) as solvent. Each of PVPh, PMA, and PMMA was dissolved in THF at a concentration of 1% (w/v). Both solutions of PVPh and PMA were mixed together at room temperature at given compositions. After stirring the mixed solution for 3 h, the solvent was allowed to evaporate at room temperature for several days. The resulting samples were finally dried under reduced pressure at a temperature of 333 K for 2 weeks. PVPh/PMMA blends and samples of pure PVPh, PMA, and PMMA were prepared in the same way.

NMR Experiment. ^{13}C CP/MAS NMR experiments were carried out on a JEOL JNM-GX270 spectrometer operating at resonance frequencies of 270 and 67.8 MHz for ^{1}H and ^{13}C, respectively. The radio-frequency field strength for both ^{1}H and ^{13}C was about 56 kHz. A double-bearing aluminum oxide rotor was used. The setting of the magic angle was monitored by the ^{79}Br NMR spectrum of KBr incorporated in the rotor. The ^{1}H decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS). ^{13}C CP/MAS spectra of the samples were measured with the standard CP/MAS pulse sequence at a magic angle sample spinning rate of about 6 kHz. The CP contact time was 1.2 ms at 310 K and 0.6 ms at 361 K. The chemical shifts of the ^{13}C spectra are reported in ppm relative to TMS by taking the methine carbon of solid adamantane (29.5 ppm) as an external reference standard. ^{1}H $T_{1\rho}$, ^{1}H T_1, and ^{13}C $T_{1\rho}$ measurements were made by the pulse sequences reported

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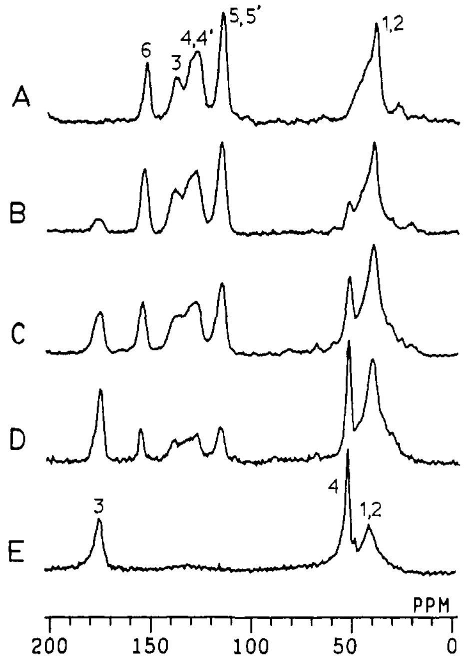


Figure 1. ^{13}C CP/MAS NMR spectra of PVPh/PMA blends at 310 K: (A) pure PVPh; (B) PVPh/PMA = 4/1; (C) PVPh/PMA = 1/1; (D) PVPh/PMA = 3/1; (E) pure PMA.

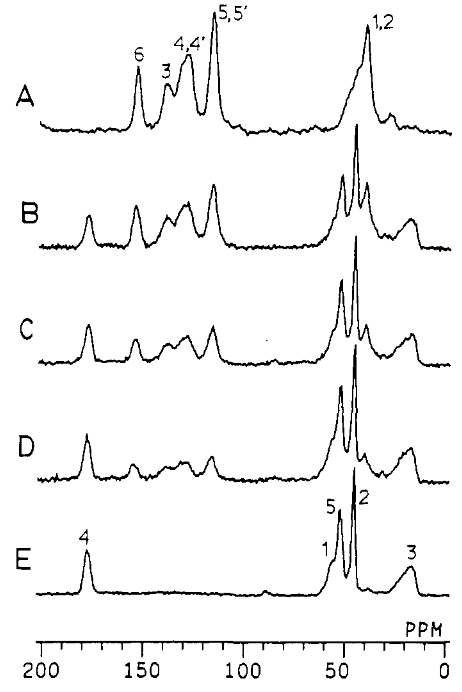


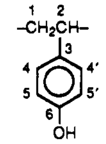
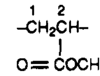
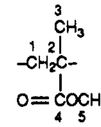
Figure 2. ^{13}C CP/MAS NMR spectra of PVPh/PMMA blends at 310 K: (A) pure PVPh; (B) PVPh/PMMA = 2/1; (C) PVPh/PMMA = 1/1; (D) PVPh/PMMA = 1/2; (E) pure PMMA.

elsewhere.[8-10] Variable-temperature measurements were accomplished by using a JEOL MVT temperature controller with an accuracy of ±1 K. Temperature calibration was done by the conventional methanol method.

Results and Discussion

^{13}C CP/MAS Spectra and Hydrogen-Bonding Interaction. ^{13}C CP/MAS spectra of PVPh/PMA and PVPh/PMMA blends at 310 K are shown in Figures 1 and 2, respectively. Assignments of ^{13}C spectra of PVPh, PMA, and PMMA were made by the reference to the previous reports[11-14] and are shown in Table I.

Table I
Assignment of ^{13}C CP/MAS Spectra of PVPh, PMA, and PMAA at 310 K

compd	*structure*	*carbon*	*assignt*
PVPh		1, 2	39.9
		3	139.3
		4, 4′	128.4
		5, 5′	115.8
		6	153.7
PMA		1, 2	41.4[a]
		3	174.9
		4	52.5
PMMA		1	56
		2	45.0
		3	16.3
		4	177.9
		5	51.9

[a] At 361 K peak 1 appears at 36.1 while peak 2 appears at 42.2 ppm.

Table II
^{13}C Chemical Shifts (ppm) of PVPh/PMA and PVPh/PMMA Blends at 310 K

	PMA or PMMA C=O	PVPh COH (C-6)	PVPh CH (C-5,5′)	PMA or PMMA OCH_3
PVPh		153.7	115.8	
PVPh/PMA = 4/1	177.3	154.3	115.8	52.5
PVPh/PMA = 2/1	176.7	154.7	115.8	52.4
PVPh/PMA = 1/1	176.1	154.7	115.8	52.5
PVPh/PMA = 1/1.5	175.6	155.4	115.8	52.5
PVPh/PMA = 1/3	175.3	155.7	115.8	52.3
PMA	174.9			52.5
PVPh/PMMA = 2/1	177.9	153.7	115.8	51.9
PVPh/PMMA = 1/1	177.9	153.7	115.8	51.9
PVPh/PMMA = 1/2	177.9	154.2	115.8	51.9
PMMA	177.9			51.9

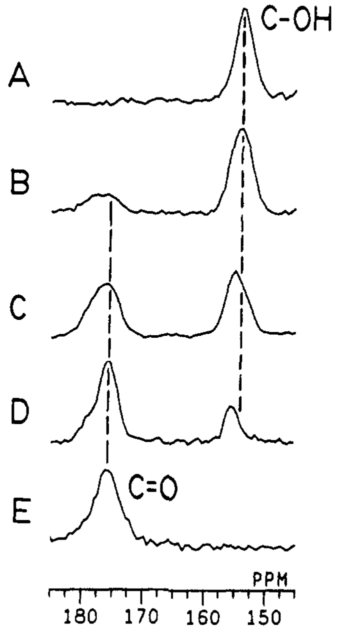


Figure 3. ^{13}C CP/MAS NMR spectra of the C=O resonance of PMA and the COH resonance of PVPh at 310 K in PVPh/PMA blends: (A) pure PVPh; (B) PVPh/PMA = 4/1; (C) PVPh/PMA = 1/1; (D) PVPh/PMA = 3/1; (E) pure PMA.

The composition dependence of the chemical shift of the resonances of several ^{13}C atoms that may participate in hydrogen bonding is summarized in Table II for PVPh/PMA and PVPh/PMMA blends at 310 K. Figure 3 shows that the isotropic chemical shifts of the COH and C=O resonances of PVPh/PMA blends vary with the composition. The COH carbon of the PVPh component resonates at 153.7 ppm for pure PVPh. The resonance shifts down-

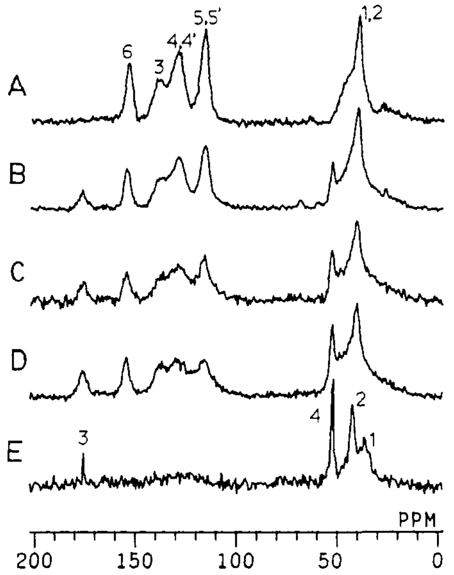


Figure 4. ^{13}C CP/MAS NMR spectra of PVPh/PMA blends at 361 K: (A) pure PVPh; (B) PVPh/PMA = 2/1; (C) PVPh/PMA = 1/1; (D) PVPh/PMA = 1/2; (E) pure PMA.

field as the PMA composition increases and appears at 155.7 ppm at PVPh/PMA = 1/3 (the maximum PMA composition studied). This is 2.0 ppm downfield relative to pure PVPh. The C═O resonance of PMA in the blends also shifts downfield as the PVPh proportion increases; the chemical shift varies from 174.9 ppm for pure PMA to 177.3 ppm for the PVPh/PMA = 4/1 blend (the maximum PVPh composition studied). This is 2.4 ppm downfield relative to pure PMA. On the other hand, other resonances of PVPh and PMA of the blends, e.g., the CH resonance (C-5,5′) of the phenolic ring of PVPh and the $-OCH_3$ resonance (C-4) of PMA, show no composition dependence.

Since strong hydrogen bonding affects the ^{13}C chemical shift of hydrogen bond participating groups,[1-4,15,16] the observed downfield shifts of the COH resonance of PVPh and the C═O resonance of PMA suggest that the intermolecular hydrogen bonding occurs between the phenolic hydroxyl proton of PVPh and the carbonyl oxygen of PMA.

^{13}C CP/MAS spectra of PVPh/PMA blends were measured also at 361 K (close to glass transition temperatures of the blends) and are shown in Figure 4. Figure 5 shows that downfield shifts of the COH resonance of PVPh and the C═O resonance of PMA are observed even at this temperature. The shift is, however, somewhat smaller than that at 310 K. The results indicate that the intermolecular hydrogen bond is still formed at higher temperatures although the interaction becomes weak.

For poly(vinyl alcohol) (PVA) blends,[2-4] the COH resonance of PVA in the miscible blends shifts upfield relative to pure PVA. As compared with the results of PVPh blends, it can be concluded that the intramolecular hydrogen-bonding interaction within pure PVA is stronger than that within pure PVPh.

Comparison of Figures 1 and 2 indicates that PVPh/PMMA blends are different from PVPh/PMA blends. The ^{13}C CP/MAS spectra of the blends have a strong resemblance to the sum of those of pure PVPh and PMMA. Apart from a 0.5 ppm downfield shift of the COH resonance of PVPh of PVPh/PMMA = 1/2, no significant change is observed (Table II). This suggests that the hydrogen bond between the two polymers is not formed or is formed so weakly that we do not observe a spectral change.

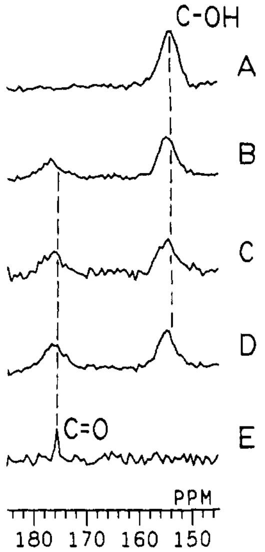


Figure 5. ^{13}C CP/MAS NMR spectra of the C═O resonance of PMA and the COH resonance of PVPh at 361 K in PVPh/PMA blends: (A) pure PVPh; (B) PVPh/PMA = 2/1; (C) PVPh/PMA = 1/1; (D) PVPh/PMA = 1/1.5; (E) pure PMA.

^1H Relaxation Time and the Miscibility. ^1H $T_{1\rho}$ values of PVPh/PMA and PVPh/PMMA blends were measured through the well-resolved ^{13}C resonances at 310 and 361 K. The results are listed in Tables III and IV. All ^{13}C resonances of pure PVPh show the same single-exponential decay in ^1H $T_{1\rho}$ and ^1H T_1 experiments at 310 K, as well as at 361 K, and so do those of pure PMMA. These results indicate that for pure PVPh and pure PMMA fast spin diffusion equalizes the relaxation rates of all protons. The situation is different for pure PMA. At 310 and 361 K different protons of PMA have different $T_{1\rho}$ values. This is attributed to the fast motion of PMA chains, which reduces the dipole–dipole interaction to a large extent. The spin diffusion becomes, therefore, too slow to equalize the relaxation times of all resonances.

For PVPh/PMA blends, all ^1H $T_{1\rho}$ values for various carbon resonances are the same at 310 K as well as at 361 K (Table III). This indicates that fast spin diffusion occurs among all protons in a range of 20–30 Å of the blends.[17,18] It can be concluded that PVPh and PMA are intimately mixed; no detectable domains on a scale of 20–30 Å are present. The similarity of $T_{1\rho}$ values indicates that intimate mixing hinders motions of both the side and main chains of PMA. The dipole–dipole interaction is not averaged out in PVPh/PMA blends. ^1H T_1 values observed through all ^{13}C resonances of each PVPh/PMA blend are found to be the same (results not shown here), also suggesting the good miscibility of the blends.

The ^1H $T_{1\rho}$ decays of PVPh/PMMA blends are not single-exponential; besides a fast main decay, there also exists a very slowly decaying component. The $T_{1\rho}$ values of the main decay component are listed in Table IV. The values of PVPh and PMMA in the blends are not the same but are quite close to those of the pure polymers. These results indicate that the two polymers are not intimately mixed and that the domain size of either the PVPh or the PMMA phase is larger than 20–30 Å. The fact that the ^1H $T_{1\rho}$ values of the two polymers become similar is ascribed to the spin–diffusion coupling occurring in the interphase between the PVPh and the PMMA phases. Although the relaxation times of the two polymers in the interphase are equalized by the effective spin–diffusion coupling, the relaxation of the whole system is not averaged out. The insufficient spin–diffusion coupling

Table III
^1H $T_{1\rho}$ (ms) of PVPh/PMA Blends at 310 and 361 K

compd	T, K	PMA C-3	PVPh C-6	PVPh C-4	PVPh C-5	PMA C-4	PVPh, PMA C-1, C-2
PVPh	310		6.9	7.1	7.2		7.2
	361		6.2	6.2	6.1		6.0
PVPh/PMA = 4/1	310	7.2	7.6	7.5	7.8		7.4
	361		4.1	4.2	4.0	4.2	4.4
PVPh/PMA = 2/1	310	8.1	7.8	8.2	8.1	8.2	8.2
	361	3.4	3.5	3.4	3.5	3.6	3.7
PVPh/PMA = 1/1	310	8.4	8.5	8.7	8.9	8.8	8.7
	361	2.8	3.0	3.1	3.0	3.2	3.2
PVPh/PMA = 1/1.5	310	13.0	12.0	12.8	12.8	12.2	12.2
	361	2.1	1.9	2.1	2.0	2.1	2.3
PVPh/PMA = 1/3	310	8.8	8.6	8.8	9.0	8.4	8.9
PMA	310	3.9				3.5	2.3
	361	1.6				2.0	1.1

Table IV
^1H $T_{1\rho}$ (ms) and T_1 (s) of PVPh/PMMA Blends at 310 K

		PMMA C-4	PVPh C-6	PVPh C-4	PVPh C-5	PMMA C-5	PMMA C-2	PVPh C-1,2	PMMA C-3
PVPh	$T_{1\rho}$		6.9	7.1	7.2			7.2	
	T_1		1.5	1.6	1.5			1.5	
PVPh/PMMA = 2/1	$T_{1\rho}$	13.7	7.7	7.8	7.7	13.6	12.5	7.5	12.2
	T_1	0.62	1.3	1.3	1.2	0.68	0.94	1.3	0.66
PVPh/PMMA = 1/1	$T_{1\rho}$	13.9	9.5	9.7	9.1	13.5	14.1	10.1	14.8
	T_1	0.76	1.3	1.3	1.3	0.74	0.73	1.2	0.72
PVPh/PMMA = 1/2	$T_{1\rho}$	14.7	7.3	7.6	8.4	13.9	14.7	9.1	13.9
	T_1	0.62	1.3	1.3	1.2	0.60	0.62	1.3	0.61
PMMA	$T_{1\rho}$	16.6				16.5	17.2		15.7
	T_1	0.51				0.52	0.50		0.53

brings about nonexponential relaxation behavior.[20,21] The ^1H T_1 study indicates that PVPh/PMMA blends are also not miscible even on a scale of 200–300 Å, because the ^1H T_1 results (Table IV) are similar to those of ^1H $T_{1\rho}$.

The results shown in the preceding section indicate that the good miscibility of PVPh/PMA blends is due to the intermolecular hydrogen bonding between PVPh and PMA. For PVPh/PMMA blends, the intermolecular hydrogen bonding is so weak that the two polymers are not miscible.

It has been found that the α-methyl group of the main chain of PMMA markedly influences the miscibility. For poly(methyl methacrylate)/poly(vinyl chloride) (PMMA/PVC) blends,[22,23] syn-PMMA forms a miscible blend with PVC, while iso-PMMA does not. They reported that this is because the hydrogen-bond-like interaction between the C=O oxygen of PMMA and the α-proton of PVC is stereochemically favored for syn-PMMA but not for iso-PMMA.[22] On the other hand, poly(methyl acrylate)/poly(vinyl chloride) forms an incompatible system.[24] We reported the miscibility of poly(vinyl alcohol)/poly(methacrylic acid) (PVA/PMAA) and poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) systems.[1,2] In aqueous solution, PVA/PMAA forms a one-to-one complex, while PVA/PAA forms a miscible blend. The α-methyl group of PMAA probably increases the hydrophobic nature of the polymer. When PVA associates with PMAA, aggregates, therefore, precipitate out from water. It was also found that methyl substituents on the benzene ring of polystyrene significantly reduce the miscibility of polystyrene/poly(2,6-dimethylphenylene oxide) blends; the effect is greater for the ortho methyl derivative than the para methyl one.[25] These results show that the polymer–polymer interaction is so subtle that even the methyl substitution can significantly alter the whole property of the blends.

Binding Effects on Molecular Motion. Relaxation Time Analysis. In most cases the motional state of the polymer is not greatly altered by blending. The proton relaxation rate (the inverse of the relaxation time) of the blends is therefore given by the proton-number average of the relaxation rates of the two polymers.[17,19,21,23] Table III shows, however, that the observed ^1H $T_{1\rho}$ values of PVPh/PMA blends at 310 K are longer than those of both pure PVPh and PMA. This means that the change in relaxation time on blending is caused not only by averaging due to proton spin diffusion but also by alteration of the motional state. Both cause the relaxation times of the component polymers in the blends to differ from those of the pure polymers. A blending effect on the motional state has been reported for poly(vinyl alcohol)/poly(vinylpyrrolidone),[3] poly(phenylene sulfide)/poly(ether sulfone),[26] and polystyrene/poly(vinyl methyl ether) blends.[27]

Further evidence of a blending effect on the motional state can be obtained from the ^{13}C $T_{1\rho}$ measurements because the low natural abundance of ^{13}C eliminates the effect of spin diffusion. ^{13}C $T_{1\rho}$ is sensitive to the motion of polymer chains in a frequency range of 10–100 kHz, which occurs below the glass transition temperature.[28,29] The ^{13}C $T_{1\rho}$ relaxation consists of two processes: spin–spin and spin–lattice relaxation. For a highly crystalline rigid polymer, the strong static proton–proton dipolar interaction makes the spin–spin process dominant in the ^{13}C $T_{1\rho}$ relaxation. In such a case, however, the ^{13}C $T_{1\rho}$ provides no information about molecular dynamics.[30] On the other hand, for amorphous glassy polymers with internal local mobility, the fluctuating dipolar fields are caused largely by the rotation of ^{13}C–^1H internuclear vectors; the spin–lattice process is dominant.[28]

Various local fields experienced by rare ^{13}C spins yield various relaxation times which are not equalized by the relatively weak spin-diffusion interaction. A multiplicity of ^{13}C $T_{1\rho}$ relaxations is therefore observed. We discuss here mainly the difference in relaxation behavior between the pure polymers and the blends.

As in most glassy polymers, the ^{13}C $T_{1\rho}$ decay of PVPh, PMA, and PMMA at 310 K is not single-exponential.

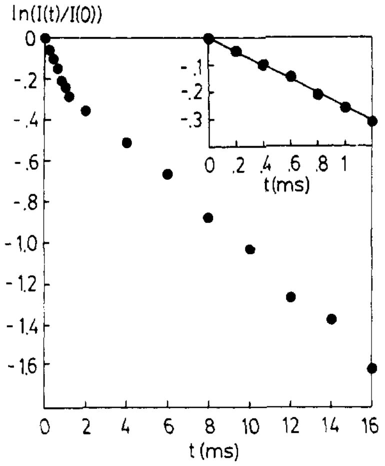


Figure 6. Signal density of the ^{13}C $T_{1\rho}$ decay of the C-5,5′ resonance of PVPh in the PVPh/PMA = 1/3 blend as a function of ^{13}C spin-locking time, t, at 310 K. The decay for a period of initially 1 ms is shown in the inset.

Figure 6 shows the ^{13}C $T_{1\rho}$ decay of the C-5,5′ resonance of PVPh in the PVPh/PMA = 1/3 blend. An average $T_{1\rho}$ determined from the initial 1-ms decay has been thought to represent a large fraction of motions at frequencies in the kilohertz range.[28] Tables V and VI summarize the average relaxation times of various carbon resonances for PVPh, PMA, PMMA, and PVPh/PMA and PVPh/PMMA blends within the initial 1-ms decay at 310 K.

When PMA is blended with PVPh, the ^{13}C $T_{1\rho}$'s of PMA in the blend become significantly longer (Table V). For example, the ^{13}C $T_{1\rho}$ value of the OCH$_3$ resonance (at 52.5 ppm) of pure PMA is only 4.7 ms; it becomes about 10 ms for most blends and 14.3 ms for the PVPh/PMA = 1/1.5 blend. A similar situation is seen for the C=O resonance of PMA in the blends. For most blends, the ^{13}C $T_{1\rho}$ value of the C=O resonance becomes very long; for a period of 16 ms of ^{13}C spin-locking time, no detectable decay can be observed. On the other hand, for PVPh, a small change in ^{13}C $T_{1\rho}$ is observed only for the COH resonance. The other resonances of PVPh in the blends retain the same relaxation characteristics as in pure PVPh. For immiscible blends of PVPh/PMMA (Table VI), there is no observable change.

These results indicate that the blending with PVPh greatly alters the motional state of PMA at lower temperatures. Blending hinders the whole segmental motion of the PMA chain. On the other hand, the blending effect on PVPh in the blend is insignificant; only the environment of the hydrogen bond is affected. The motional states of the two polymers in PVPh/PMMA blends are not affected at all by blending.

On the basis of strong spin-diffusion coupling, the proton relaxation time of the blend ($T_{1\rho}$) can be written as[17,19,21,23]

$$T_{1\rho}^{-1} = (N_1/N)T_{1\rho}(1)^{-1} + (N_2/N)T_{1\rho}(2)^{-1} \qquad (1)$$

where $T_{1\rho}(1)$ and $T_{1\rho}(2)$ denote the relaxation times of component polymers 1 and 2, respectively. N_1 and N_2 are the numbers of protons of the respective components, and N is the total number of protons: $N = N_1 + N_2$.

Since at lower temperatures the motional state of PVPh in the blends hardly changes (^{13}C $T_{1\rho}$ results), we assume that at 310 K the value of $T_{1\rho}(1)$ in eq 1 (PVPh in the blends) is the same as that of the pure PVPh (7.1 ms). The value of $T_{1\rho}(2)$ in eq 1 (PMA in the blend) is estimated by eq 1. $T_{1\rho}(2)$ values for PVPh/PMA = 4/1, 2/1, 1/1, 1/1.5, and 1/3 blends are 12, 13, 12, 38.6, and 10 ms, respectively. These values are longer than those of pure PMA, indicating that the motional state of PMA in the blends is altered by blending.

A similar evaluation was made for ^{1}H $T_{1\rho}$ of PVPh/PMA blends at 361 K. The $T_{1\rho}(2)$ values of PVPh/PMA = 4/1, 2/1, 1/1, and 1/1.5 blends at 361 K are 1.6, 1.6, 1.7, and 1.3 ms, respectively. These values are comparable to the value observed for the C=O resonance of pure PMA (which is considered as a relaxation time averaged over the whole pure PMA), suggesting that blending does not affect the motional state of PMA at 361 K very much.

It is worth noting that the ^{1}H $T_{1\rho}(2)$ value of PMA is longer for the PVPh/PMA = 1/1.5 blend. Similarly, a longer value is found in the ^{13}C $T_{1\rho}$ of the C-4 resonance of PMA in the blends (Table V). The blending effect on the molecular motion of PMA at this composition seems greater than those of the others.

Blending Effects on Molecular Motion. ^{13}C Line-width Analysis. The glass transition temperature (T_g) is an important parameter for studying chain motion. It represents onset of large-scale segmental motion of the polymer chain. Measurement of the ^{13}C line width of the CP/MAS spectra provides information about molecular motion. A line narrowing of the ^{13}C CP/MAS spectra followed by a line broadening occurs owing to the onset of segmental motion as the temperature increases above T_g.[31] If two different polymers in the blend are intimately mixed together, segmental motions of both polymers interfere with each other. A miscible blend often shows a single glass transition at a temperature representing the weight-averaged T_g's of two polymers, although the chain dynamics of the component polymers may still have a different characteristic temperature dependence. The effect is observable when the glass transition temperatures of two polymers are different.

The ^{13}C CP/MAS spectra at various temperatures for the PVPh/PMA = 1/1.5 blend, of which the blending effect on motion is very noticeable, are shown in Figure 7. Above 323 K the carbon resonances of PVPh in the blend become broader as the temperature increases, while those of PMA become narrower. At the much higher temperature of 394 K, the line width of the aromatic carbon resonances of PVPh in the blends is very broad; the three peaks at about 138, 130, and 116 ppm at lower temperatures coalesce to one broad line. The C-6 resonance at about 155 ppm and the C-1,2 resonance at 40 ppm of PVPh also become broader with increasing temperature. In contrast, the C-3 and the C-4 resonances of PMA in the blends become narrower with increasing temperature. The similar temperature dependence of the ^{13}C line width was reported for polystyrene/poly(vinyl methyl ether) (PS/PVME) blends.[31] PVPh/PMA and PS/PVME blends resemble each other; both blends consist of polymers with higher (PVPh and PS) and lower (PMA and PVME) glass transition temperatures.

Because of the limited temperature range studied here, we observe only the line-broadening part of PVPh in the blends and the line-narrowing part of PMA. For pure PVPh, the line broadening is expected to occur above 393 K (T_g of PVPh). The broadening is, however, observed even at 323 K for PVPh in the blends. For PMA in the blends, the line width at 394 K is even broader than that of pure PMA at 361 K (Figure 5). These results show that molecular motions of the two polymers in the blends differ substantially from those of each pure polymer. The motions of the two polymers are correlated to a great extent but not completely concerted.

Table V
^{13}C $T_{1\rho}$ Values (ms) of PVPh/PMA Blends at 310 K

	PMA C-3	PVPh C-6	PVPh C-4	PVPh C-5	PMA C-4	PVPh, PMA C-1, C-2
PVPh		7.3	4.9	4.3		4.0
PVPh/PMA = 4/1	10.5	16.3	4.7	4.4	9.2	3.8
PVPh/PMA = 2/1	very long[a]		4.8	4.4	9.5	4.9
PVPh/PMA = 1/1	very long[a]		4.9	4.2	10.3	5.0
PVPh/PMA = 1/1.5	very long[a]		5.0	4.5	14.3	5.2
PVPh/PMA = 1/3	very long[a]		4.8	4.4	10.5	4.0
PMA	6.3				4.7	2.0

[a] Even for a period of 16 ms of ^{13}C spin-locking time, no detectable decay can be observed.

Table VI
^{13}C $T_{1\rho}$ Values (ms) of PVPh/PMMA Blends at 310 K

	PMMA C-4	PVPh C-6	PVPh C-4	PMMA C-1	PMMA C-5	PMMA C-1	PMMA C-2	PVPh C-1,2	PMMA C-3
PVPh		7.3	4.9	4.3				4.0	
PVPh/PMMA = 2/1	11.3	7.4	4.8	4.4	1.5	8.0	10.4	3.8	12.9
PVPh/PMMA = 1/1	11.0	7.5	4.8	4.3	1.5	8.2	10.2	3.9	12.4
PVPh/PMMA = 1/2	11.6	7.2	4.9	4.5	1.6	8.1	11.4	4.1	13.0
PMMA	11.5				1.6	8.2	11.7		13.2

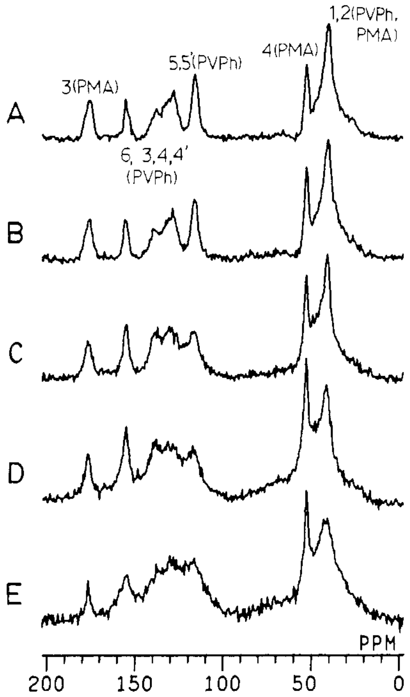


Figure 7. ^{13}C CP/MAS spectra of the PVPh/PMA = 1/1.5 blend at various temperatures: (A) at 310 K; (B) at 339 K; (C) at 361 K; (D) at 383 K; (E) at 394 K.

In addition to the temperature dependence, the composition dependence of the ^{13}C line width is worth noting. As seen in Figures 3 and 5, at 310 K the line width of the C=O resonance is 340 Hz for pure PMA, about 400 Hz for the PVPh/PMA = 2/1 blend, and 450 Hz for the PVPh/PMA = 4/1 blend. For the COH resonance of PVPh, the line width is 240 Hz for pure PVPh, 280 Hz for the PVPh/PMA = 1/1 blend, and 190 Hz for the PVPh/PMA = 1/3 blend. It is found that the line width of PMA at 361 K becomes noticeably broadened in the blends as compared to pure PMA (Figure 4). The line width of the C=O resonance of PMA is 40 Hz in pure PMA but more than 350 Hz in the blends. The resonances of PVPh are not affected as remarkably as those of PMA in the blends.

The resonances of the COH of PVPh and the C=O of PMA at lower temperatures consist of a group of peaks corresponding to non-hydrogen-bonded, weakly hydrogen-bonded, and strongly hydrogen-bonded resonances. Because the chemical shift difference of these peaks is smaller than the line width, they appear as a single line at the weighted-average chemical shift position. As the intensity of the downfield peak increases, the line width of the peaks also becomes broad. A similar phenomenon was reported for poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP) blends.[3]

At higher temperatures, not only the distribution of various hydrogen-bonding states but also the blending effect on motion should be taken into account. Polymer chains of pure PMA are in the rubbery state at room temperature. At a high temperature of 361 K, the fast isotropic motion of the polymer chains brings about liquidlike narrow peaks for pure PMA. When associated with "hard" PVPh chains, the molecular motion of PMA is greatly restricted by the steric hindrance of PVPh. The intermolecular hydrogen bonding also significantly limits the freedom of molecular motions. Thus, these effects bring about an additional line broadening for PMA in the blends. For PMA-rich blends, the line width of PVPh is somewhat narrowed, owing to such motional effects even at 310 K. The results provide additional evidence for blending effects on molecular motions.

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References and Notes

(1) Zhang, X.; Takegoshi, K.; Hikichi, K. *Polym. J.* **1991**, *23*, 79.
(2) Zhang, X.; Takegoshi, K.; Hikichi, K. *Polym. J.* **1991**, *23*, 87.
(3) Zhang, X.; Takegoshi, K.; Hikichi, K. *Polymer*, in press.
(4) Zhang, X.; Takegoshi, K.; Hikichi, K. *Polymer*, in press.
(5) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1984**, *17*, 1671.
(6) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.
(7) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(8) Axelson, D. E.; Russell, K. *Prog. Polym. Sci.* **1985**, *11*, 221.
(9) Suilivan, M. J.; Maciel, G. E. *Anal. Chem.* **1982**, *54*, 1615.
(10) Wang, Y.; Chen, Q.; Zhang, X. *Interfaces in Polymer, Ceramic, and Metal Matrix Composites*; Ishida, H., Ed.; Elsevier Press: New York, 1988; p 249.
(11) Sojka, S. A.; Wolfe, R. A.; Dietz, E. A., Jr.; Dannels, B. F. *Macromolecules* **1979**, *12*, 767.
(12) Fyfe, C. A.; Rudin, A.; Tchir, W. J. *Macromolecules* **1980**, *13*, 1322.

(13) Dhal, P. K.; Babu, G. N.; Nanda, R. *Macromolecules* **1984**, *17*, 1131.

(14) Edzes, H. T. *Polymer* **1983**, *24*, 1425.

(15) VanderHart, D. L.; Earl, W.; Garroway, A. N. *J. Magn. Reson.* **1981**, *16*, 295.

(16) Grobelny, J.; Rice, D. M.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1990**, *23*, 2139.

(17) McBrierty, V. J.; Douglass, D. C.; Kwei, T. *Macromolecules* **1978**, *11*, 1265.

(18) VanderHart, D. L. *Makromol. Chem., Macromol. Symp.* **1990**, *34*, 125.

(19) Zhang, X.; Qiu, L.; Wang, D.; Wang, Y. *Chin. J. Polym. Sci.* **1988**, *6*, 159.

(20) Tanaka, H.; Nishi, T. *Phys. Rev. B* **1986**, *33*, 32.

(21) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.

(22) Schurer, J. W.; de Boer, A.; Challa, G. *Polymer* **1975**, *16*, 201.

(23) Albert, B.; Jérôme, R.; Teyssié, P.; Smyth, G.; Boyle, N. G.; McBrierty, V. J. *Macromolecules* **1985**, *18*, 388.

(24) Kern, R. J. *J. Polym. Sci.* **1958**, *33*, 524.

(25) Dickinson, L. C.; Yang, H.; Chu, C.-W.; Stein, R. S.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1757.

(26) Zhang, X.; Wang, Y. *Polymer* **1989**, *30*, 1867.

(27) Chu, C.-W.; Dickinson, L. C.; Chien, J. C. W. *J. Appl. Polym. Sci.* **1990**, *41*, 2311.

(28) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

(29) Andreis, M.; Koenig, J. L. *Adv. Polym. Sci.* **1989**, *89*, 69.

(30) VanderHart, D. L.; Garroway, A. N. *J. Chem. Phys.* **1979**, *71*, 2773.

(31) Takegoshi, K.; Hikichi, K. *J. Chem. Phys.* **1991**, *94*, 3200.

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