

Miscibility of Poly(vinyl alcohol)/Poly(methacrylic acid) and Poly(vinyl alcohol)/Poly(acrylic acid) Systems

II. High-Resolution Solid-State CP/MAS ^{13}C NMR Studies

Xiaoqing ZHANG,* K. TAKEGOSHI, and Kunio HIKICHI

*NMR Laboratory and Department of Polymer Science, Faculty of Science,
Hokkaido University, Sapporo 060, Japan*

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ABSTRACT: Miscibility of poly(vinyl alcohol)/poly(methacrylic acid) complexes and poly(vinyl alcohol)/poly(acrylic acid) blends is investigated by high-resolution ^{13}C solid-state NMR method. Observed ^{13}C spectra are discussed in terms of hydrogen-bonding effects on chemical shift. The results indicate that poly(vinyl alcohol) and poly(methacrylic acid) are intimately mixed on a scale of 20–30 Å due to intermolecular hydrogen bonding to form equimolar-ratio complexes. For the poly(vinyl alcohol)/poly(acrylic acid)=1/1 blend, the two polymers are also miscible, the crystalline phase of PVA is destroyed completely and no detectable domain can be observed for the blend on a scale of 20–30 Å. Poly(vinyl alcohol)/poly(acrylic acid)=2/1 and 1/2 blends are homogenous on a scale of 200–300 Å, but heterogeneous on a smaller scale.

KEY WORDS Poly(vinyl alcohol) / Poly(methacrylic acid) / Poly(acrylic acid) / High-Resolution ^{13}C Solid-State NMR / Polymer Blends / Polymer Complexes / Miscibility / Hydrogen-Bonding Interaction / Morphology /

For two dissimilar polymers to be miscible, some exothermic intermolecular interactions should occur. Among many possible interactions, the hydrogen-bonding interaction has been studied extensively in recent years.^{1–6} High-resolution ^{13}C solid-state NMR is particularly useful for investigating hydrogen-bonding interaction. Helpful information about the hydrogen bonding can be obtained through characteristic downfield shifts of ^{13}C nuclei participating in hydrogen bonding.^{7,8} Although such downfield shift induced by hydrogen bonding in solution reflects an average of bonded and non-bonded states, a rigid structure of hydrogen bonding in the solid state would cause further downfield shift.^{9,10} Furthermore, the high-resolution ^{13}C solid-state NMR method enables us to measure the relaxation time of ^1H spins of individual

components of polymers through well-resolved ^{13}C signals and to examine the domain structure and miscibility of polymer blends in the solid state. If polymer chains are intimately mixed, fast spin diffusion among ^1H spins equalizes spin-lattice relaxation times of all protons. On the other hand, if the domain size of multi-phase structure of polymer blends is larger than the characteristic spin diffusion path length, the relaxation time can be observed separately for each component of polymers.^{11–18}

In this work, we examine the hydrogen-bonding interaction and miscibility of poly(vinyl alcohol)/poly(methacrylic acid) (PVA/PMAA) and poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) systems. Since PVA, PMAA, and PAA all have strong hydrogen-bonding donors and acceptors, there would be inter-

* On leave from Analytical Center, East China Normal University, Shanghai, P. R. China.

molecular hydrogen bonds between two different polymers as well as intramolecular and intermolecular hydrogen bonds among the same kinds of individual polymers. The high-resolution proton NMR study of PVA/PMAA and PVA/PAA systems in dimethyl sulfoxide (DMSO) solution has been reported in the preceding paper,¹⁹ in which the interaction between PVA and PMAA or PAA was observed. It was suggested that the different polymer chains are mixed on a scale less than 4 Å. In this paper, we provide some information about intermolecular hydrogen bonding between two different polymers in the solid state by ¹³C CP/MAS NMR techniques. The domain structure and miscibility of PVA/PMAA and PVA/PAA systems on a scales of 20–30 Å to 200–300 Å were also investigated by measuring the ¹H spin-lattice relaxation times both in rotating ($T_{1\rho}$) and laboratory frames (T_1).

EXPERIMENTAL

The molecular weight of PVA is 110,000, and those of PMAA and PAA are 40,000–70,000 and 20,000–40,000, respectively.

PVA and PAA were mixed in aqueous solution at pH=2 in compositions of 2/1, 1/1, and 1/2 in monomer-units. The homogeneously mixed solutions were obtained. After stirring the mixed solutions for 5 h, the solvent was allowed to evaporate at room temperature for several days and the transparent films were obtained after further drying under reduced pressure at 323 K for 3 days.

PVA/PMAA samples were prepared by mixing 0.12 wt% aqueous solutions of PVA and PMAA in monomer-units of 1/2 and 2/1 at pH=2. Prowderish solids appeared as soon as the two solutions were mixed. The mixtures were stirred for one day and then allowed to stand for 20 h to precipitate the powder solids completely. The solids were filtered, washed and dried under reduced pressure at 323 K for 3 days. The composition of the resulting

samples was found to be 1.1/1.0 for both mixtures, as previous reported.¹⁹ We denote these samples as PVA/PMAA complexes **1** and **2**.

NMR experiments were carried out on a JEOL JNM-GX270 spectrometer operating at resonance frequencies of 270 and 67.8 MHz for ¹H and ¹³C, respectively. High-resolution ¹³C NMR was realized by magic-angle sample spinning (MAS) and high-power spin decoupling. To enhance the signal-to-noise ratio, the crosspolarization (CP) technique was applied. ¹H decoupling frequency was chosen to be 3 ppm downfield from tetramethylsilane (TMS). A double-bearing aluminum oxide rotor was used and the setting of the magic angle was monitored by the ⁷⁹Br NMR spectrum of KBr incorporated in the rotor.²⁰ The contact time for CP was 1 ms and the radio-frequency (rf) field strength for both ¹H and ¹³C was about 56 KHz. ¹HT_{1ρ} and T_1 measurements were made by methods reported elsewhere.^{12,21} The chemical shifts of ¹³C spectra are reported in ppm relative to TMS by taking the methine carbon of solid adamantane (29.50 ppm) as an external reference standard. Variable-temperature measurements were accomplished using a JEOL MVT temperature controller. Temperature calibration was done by the conventional methanol method.²²

RESULTS AND DISCUSSION

The ¹³C CP/MAS spectra of PVA, PMAA, and PVA/PMAA complexes and PVA/PAA blends were measured at various temperatures from 311 to 383 K. No remarkable temperature dependence of the spectra was found in this temperature range. The CP/MAS spectra of PVA, PMAA, and PVA/PMAA complexes at a temperature of 311 K are shown in Figure 1. The spectra of PVA, PAA, and PVA/PAA blends at 311 K are shown in Figure 2. Bars in the figures indicate ¹³C peak positions observed in DMSO-*d*₆ solution at a temperature of

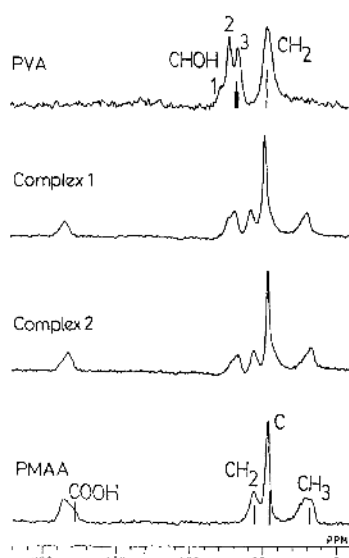


Figure 1. ^{13}C CP/MAS spectra of PVA, PMAA and PVA/PMAA complexes at 311 K. Bars indicate peak positions in $\text{DMSO}-d_6$ solution at 363 K.

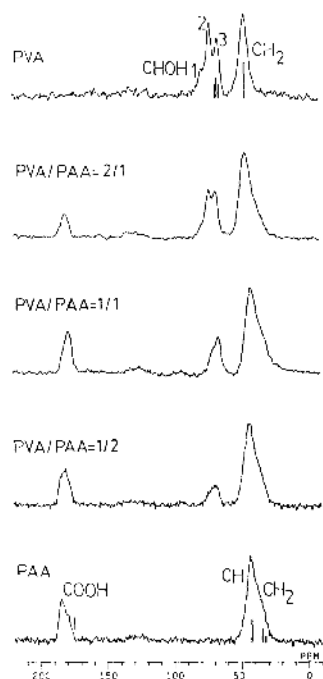


Figure 2. ^{13}C CP/MAS spectra of PVA, PAA and PVA/PAA blends at 311 K. Bars indicate peak position in $\text{DMSO}-d_6$ solution at 363 K.

363 K. Peak assignments were based on previous results^{23–27} and shown in the spectra.

Resonances of COOH carbons of PMAA and PAA and of CHOH carbon of PVA whose chemical shifts are very sensitive to hydrogen bond formation consist of well-resolved peaks without any overlapping for all samples. For pure PVA, CHOH carbon shows three peaks in the solid state as previously reported.²³ In solution, three peaks were also observed, reflecting *mm*, *mr*, and *rr* triads. The three CHOH peaks (1, 2, and 3) in the solid state appear at lower fields as compared to the triad resonances in solution. Terao *et al.* interpreted such downfield shifts of CHOH resonances in the solid state in terms of intramolecular hydrogen bonding. They assigned peak 1 of CHOH peaks to the *mm* triad of CHOH which is hydrogen bonded to both the two nearest neighbors, peak 2 to *mm* and *mr* hydrogen bonded to one of the nearest neighbors, and peak 3 to *mm*, *mr*, and *rr* not hydrogen-bonded at all.²³ Thus, peaks 1 and 2 can be taken as indicators of intramolecular hydrogen bonding of OH groups between two consecutive units of PVA.

For pure PMAA and PAA, line-broadening masks the tacticity splitting of the solid-state spectra. Apart from the broadening, significant downfield shifts of 4–6 ppm were found for COOH carbons in the solid state as compared to those in solution. These downfield shifts would be attributed to hydrogen-bonding enhancement in the rigid solid state.

For PVA/PMAA complexes, the intensities of peaks 1 and 2 of CHOH carbon resonance decrease significantly. The three-peak characteristic of CHOH carbon disappears completely, and the whole resonance becomes a single broad peak at about 67.5 ppm. The COOH carbon of PMAA moves to upfield by about 3 ppm relative to that of pure PMAA.

For PVA/PAA blends, a remarkable composition-dependence of the ^{13}C spectra was observed. For PVA/PAA=2/1 sample, the spectrum still retains the three-peak character-

istic, although the intensities of peaks 1 and 2 of the CHOH carbon of PVA decrease noticeably as compared to those of pure PVA. For PVA/PAA=1/1 and 1/2, peaks 1 and 2 become much smaller, and the three-peak characteristic almost disappears. The resonance appears as a single broad line at about 67 ppm. Furthermore, upfield shift of the COOH peak of PAA of 2.7 ppm relative to pure PAA was found for PVA/PAA=2/1 and 1/1 blends. For PVA/PAA=1/2, the COOH peak of PAA appears at 180.3 ppm; the shift difference from that of pure PAA is less as compared to those of PVA/PAA=1/1 and 1/2 blends.

It was reported that if PVA and PMAA are mixed in water solution, white powder is precipitated, and the composition of the precipitates is close to 1/1, irrespective of the initial mixing ratio of PVA and PMAA. Thus, it is suggested that PVA/PMAA forms a complex. The constancy of the composition was confirmed in this work. Therefore, it will be suggested that the interaction undergoing in PVA/PMAA complex is possibly the intermolecular hydrogen bonding between OH and COOH groups, as suggested previously.^{28,29} Since peaks 1 and 2 of CHOH carbon of PVA component are indicators of the intramolecular hydrogen bonding between the two consecutive units, the decrease in intensities of peaks 1 and 2 is probably attributable to the dissociation of the intramolecular hydrogen bonds between the two consecutive units of PVA. The upfield shift of COOH resonance of PMAA may imply a break of intramolecular hydrogen bonding on complex formation with PVA.

The composition-dependent ¹³C spectra of PVA/PAA blends can be interpreted in terms of the dissociation of intramolecular hydrogen bonds. When PVA is rich in the system, the equivalent amount of PVA to PAA breaks the intramolecular hydrogen bonding to form miscible blends with PAA and excess PVA still retains intramolecular hydrogen bonding. The

observed CHOH peak reflects the sum of two species, the three-peak characteristic with decreased intensity of peaks 1 and 2 and increased intensity of peak 3 of CHOH carbon. The upfield shift of COOH carbon was also observed simultaneously. For PAA rich blend, the situation is just contrary; the dissociation of the intramolecular hydrogen bonds among PVA chains destroys the three-peak characteristic of CHOH carbon signal while the excess PAA shows little change in COOH carbon signal.

For polymer blends, it is important to know how homogeneously two different polymers are miscible. The intermolecular hydrogen bonding between two different polymers should cause the systems to be microscopically homogenous. ¹H *T*_{1ρ} and ¹H *T*₁ as measured through ¹³C resonance by CP/MAS techniques provide useful information about domain size; typically ¹H *T*_{1ρ} gives information on a scale of 20–30 Å, and *T*₁ on a scale of 200–300 Å.^{30–32} We measured ¹H *T*_{1ρ} values of PVA, PMAA, and PAA at three different temperatures and the data are listed in Table I. It was

Table I. ¹H *T*_{1ρ} values (ms) of PVA, PMAA, and PAA at various temperatures^a

PVA	CHOH (76.9, 71.2, 64.9 ppm)		CH ₂ (43.5 ppm)	
311 K	3.5 (43%)	9.6 (57%)	3.8 (46%)	9.7 (54%)
339 K	2.4 (56%)	11 (44%)	2.5 (51%)	11 (49%)
383 K	2.5 (54%)	10 (46%)	2.3 (53%)	11 (47%)
PMAA	COOH (185.6 ppm)	CH ₂ (55.7 ppm)	C (46.2 ppm)	CH ₃ (20.1 ppm)
311 K	7.0	7.2	7.6	6.7
339 K	7.2	7.9	7.5	7.4
383 K	4.9	5.5	5.1	5.1
PAA	COOH (182.2 ppm)		CH, CH ₂ (41.5 ppm)	
331 K	6.5		6.9	
339 K	4.3		4.2	
383 K	3.8		3.9	

^a PVA shows two components, and values in parentheses represent percentages of two components.

Table II. ^1H $T_{1\rho}$ values (ms) of PVA/PMAA and PVA/PAA systems at 339 K^a

	COOH	CHOH
PMAA	7.2	
PVA/PMAA complex 1	3.3	3.2
PVA/PMAA complex 2	3.1	3.2
PVA		2.4 (56%), 11 (44%)
PVA/PAA = 2/1	4.3	2.5 (49%), 10 (51%)
PVA/PAA = 1/1	2.8	2.8
PVA/PAA = 1/2	5.3	2.4 (54%), 11 (46%)
PAA	4.3	

^a PVA and PMAA component in PVA/PAA = 2/1 and 1/2 blends show two components, and values in parentheses show percentages of the two components.

found that at 339 K the value of PVA differs much from those of PMAA and PAA. Therefore, the ^1H $T_{1\rho}$ at 339 K was measured for PVA/PMAA and PVA/PAA systems (Table II) to study their miscibility.

All carbon resonances of a pure PMAA sample show an identical single-exponential decay with ^1H spin-locking time in the $T_{1\rho}$ experiments, indicating that the fast spin diffusion among protons equalizes the relaxation time of all protons. Similar results were obtained for pure PAA.

On the other hand, all carbon resonances of PVA show non-exponential ^1H $T_{1\rho}$ decay, which can be decomposed into two-exponential components. With increasing temperature, the fast component relaxes more rapidly, while the slow component does not show any remarkable change. Since PVA is a semi-crystalline polymer and the amorphous phase would not be observed by CP techniques because of the weak CP ability²³ and short proton $T_{1\rho}$, the slow decay component would be attributed to crystalline phase, and the fast component to an intermediate phase. Because of the different CP ability between different phases, the ratio of each component does not correspond to the composition of each phase.

For PVA/PMAA complexes, it is worth noting that ^1H $T_{1\rho}$ values for PMAA (observed from the COOH peak) and for PVA (observed

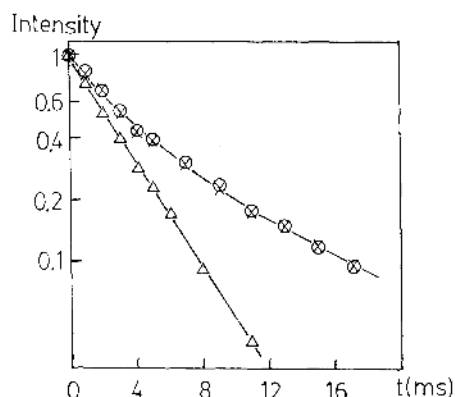


Figure 3. ^1H $T_{1\rho}$ decays of pure PVA (\times) and PVA components (observed from CHOH peak of PVA) in PVA/PAA = 2/1 (\circ) and PVA/PAA = 1/1 (Δ) blends, in which the intensity of ^{13}C resonance is plotted against ^1H spin-locking time (t).

from the CHOH peak) are the same at a temperature of 339 K. These results suggest that the spin diffusion among protons of the complex systems is very fast. PVA and PMAA are mixed so intimately that there would be strong dipolar dipolar interaction between different polymers which cause the strong spin-diffusion coupling interaction between different polymers. Intimate mixing would be caused by the intermolecular hydrogen bonding between PVA and PMAA. No detectable domain can be observed on a scale less than the characteristic spin diffusion path length involved in the $T_{1\rho}$ measurement. The crystalline phase of PVA also does not exist in PVA/PMAA complexes. The observed $T_{1\rho}$ values of complexes were found to be the average of the values of pure PMAA and amorphous PVA.

Figure 3 shows the ^1H $T_{1\rho}$ decays of the CHOH resonances for pure PVA and PVA components in PVA/PAA = 2/1 and PVA/PAA = 1/1 blends, in which the intensity of carbon resonance is plotted against the ^1H spin-locking time. The ^1H $T_{1\rho}$ decay of PVA/PAA = 1/1 blend is also single exponential as similarly as that of PVA/PMAA complexes, suggesting that PVA/PAA = 1/1

blends form a uniform phase. No detectable domains exist on a scale of 20–30 Å. $T_{1\rho}$ decays of PVA component of PVA/PAA=2/1 and 1/2 blends are identical to that of pure PVA and $T_{1\rho}$ values of PAA observed from the COOH peak are almost the same as or somewhat larger than those of pure PAA. This implies that on a scale of 20–30 Å the miscibility of both PVA/PAA=2/1 and 1/2 blends are poor. PVA component in the blends has a similar domain structure as that of pure PVA. In general, the miscibility for crystalline-amorphous blends would be better in an amorphous-component rich system than that of crystalline-component rich system, such as poly(vinylidene fluoride)/poly(methyl methacrylate),¹⁵ poly(phenylene sulphide)/poly(ether sulphone),¹⁶ poly(vinylidene fluoride)/poly(ethyl methacrylate),³³ and poly(phenylene sulphide)/polystyrene.³⁴ It is of interest to note that for PVA/PAA blends, even in the amorphous component rich system of PVA/PAA=1/2, miscibility is still poor.

To explore miscibility on a somewhat larger scale (200–300 Å), ^1H T_1 of PVA/PAA blends was measured at a temperature of 311 K and the results are summarized in Table III. Only a single T_1 value for each sample can be observed, showing that not all domains are detected on this scale. The domain sizes of semi-crystalline PVA and multi-component PVA/PAA blends are all smaller than 200–300 Å, and the T_1 values observed would be the average of T_1 of all components. On the

basis of strong spin-diffusion coupling, the average relaxation time of two-component system can be given as^{30–32}

$$T_1^{-1} = (N_1/N)T_{1(1)}^{-1} + (N_2/N)T_{1(2)}^{-1}, \quad (1)$$

where $T_{1(1)}$ and $T_{1(2)}$ denote the observed relaxation times of pure components 1 and 2 with N_1 and N_2 protons, respectively, and N is the total number of protons in the system, $N = N_1 + N_2$. The calculated values (shown in Table III as calcd) are in good agreement with the experimental values. This indicates that PVA/PAA blends are completely miscible on a scale of 200–300 Å. In general, the physical properties of crystalline-amorphous blends are highly dependent on crystallinity and the properties of the crystalline component in the blends. For PVA/PAA blends, morphology can be controlled by changing the composition of blends. This is beneficial for using high performance polymer blends.

CONCLUSION

When PVA is mixed with PMAA to form equimolar ratio complexes, the intermolecular hydrogen bonding between PVA and PMAA causes homogenous mixing of the two polymers. No detectable domain can be observed on a scale of 20–30 Å for PVA/PMAA complexes. For PVA/PAA=1/1 blend, the same conclusion can be reached as that for PVA/PMAA complexes. When either PVA or PAA is rich in the blends, the two polymers are miscible on a scale of 200–300 Å, but the blends are heterogeneous on a smaller scale.

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Table III. ^1H T_1 values (s) of PVA/PAA blends at 311 K

	COOH	CHOH	CH ₂ or CH	Calcd ^a
PVA		7.3	7.2	7.3
PVA/PAA=2/1	5.6	5.9	5.8	5.9
PVA/PAA=1/1	5.3	5.3	5.2	5.3
PVA/PAA=1/2	3.4	3.6	3.6	4.5
PAA	3.1		3.0	3.1

^a Calculated values from eq. 1 (see the text).

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