# High-resolution solid-state $^{13}$C nuclear magnetic resonance study on poly(vinyl alcohol)/poly(vinylpyrrolidone) blends

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The miscibility and domain structure of poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP) blends are investigated by high-resolution solid-state $^{13}$C nuclear magnetic resonance methods. The observed $^{13}$C spectra and the intermolecular cross-polarization of the blends suggest a hydrogen-bonding interaction between the two polymers. $^1$H $T_1$ and $T_{1\rho}$ results indicate that the blends are miscible at all compositions on a scale of 200–300 Å. On a scale of 20–30 Å, however, the miscibility of the blends depends significantly on the composition. When the PVA composition is more than 46 wt%, the blends are composed of two phases, an amorphous miscible phase of PVP plus PVA and a pure PVA phase. The crystallinity of the PVA phase decreases rapidly with decreasing PVA composition. When the PVA composition is less than 46 wt%, the blend is completely miscible. The composition of PVA phase in the blends was inferred from the results of $^1$H $T_{1\rho}$.

**(Keywords: poly(vinyl alcohol); poly(vinylpyrrolidone); polymer blends; high-resolution solid-state $^{13}$C nuclear magnetic resonance; domain structure; hydrogen-bonding interaction)**

## INTRODUCTION

In the course of our investigation of the structure of polymer blends in which hydrogen bonding is a dominant intermolecular interaction[1], we studied the miscibility and domain structure of poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP) blends.

PVA is a semicrystalline polymer with a melting temperature $T_m$ of 503 K for the crystalline part and a glass transition temperature $T_g$ of 358 K for the amorphous part. PVP is a highly amorphous polymer with $T_g$ of 423 K. The two polymers are dissimilar in both chemical structure and physical properties. The two polymers are water-soluble and have polar side-groups; PVP contains a pyrrolidone ring, which has a proton-accepting carbonyl group, and PVA contains a hydroxyl proton. It is therefore expected that a hydrogen-bonding interaction would occur between PVA and PVP. Such an interaction brings about the thermodynamic miscibility of the blends and affects the morphology of component polymers[2,3].

There have been a few reports dealing with the preparation of PVA/PVP blend films[4] and fibres[5] from aqueous solution. Recently, Nishio *et al.* studied in detail the miscibility of PVA/PVP blends by differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffraction (WAXD)[6]. They reported that only a single glass transition occurs at all compositions studied, and that the crystallinity of PVA decreases remarkably with decreasing PVA composition. The melting and crystallization temperatures of PVA observed in d.s.c. heating and cooling processes decrease systematically with decreasing PVA composition. These results indicate that the PVA/PVP polymer pair was thermodynamically miscible. The negative value of the polymer–polymer interaction parameter obtained from the melting-point depression analysis suggests that the good miscibility of PVA/PVP can be attributed to hydrogen bonding between the hydroxyl and carbonyl groups.

High-resolution solid-state $^{13}$C n.m.r. is a powerful method for investigating both the intermolecular hydrogen-bonding interaction and the miscibility of polymer blends. Strong hydrogen bonding would alter the $^{13}$C chemical shift of hydrogen-bond participating groups[1,7,8]. The cross-polarization/magic-angle sample spinning (CP/MAS) solid-state $^{13}$C n.m.r. method also enables us to investigate the domain structure. The miscibility of polymer blends in the solid state can be studied on a scale of less than 10 Å, of 20–30 Å, or of 200–300 Å by measuring the $^1$H/$^{13}$C cross-polarization rate and the $^1$H relaxation time of each polymer component of the blends through the well resolved $^{13}$C resonance[9–17].

The purpose of this work is to obtain n.m.r. evidence of intermolecular hydrogen-bonding interaction between PVA and PVP and information about the morphology and miscibility of the blends. $^{13}$C CP/MAS spectra and the intermolecular cross-polarization behaviour of the blends are observed to study the hydrogen bonding between the two polymers. The composition dependences of $^1$H $T_{1\rho}$ and $T_1$ values are interpreted in terms of the domain structure and miscibility.

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**Table 1** The composition of PVA/PVP blend samples in weight ratio[a]

| Samples | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| PVA/PVP | 89/11<br>(20/1) | 81/19<br>(10/1) | 72/28<br>(6/1) | 56/44<br>(3/1) | 46/54<br>(2/1) | 30/70<br>(1/1) | 17/83<br>(2/1) |

[a] PVA/PVP molar ratios are indicated in parentheses

## EXPERIMENTAL

### *Samples*

PVA was kindly provided by Kuraray Co. Ltd. Its molecular weight is 110000. PVP with a molecular weight of 40000 was obtained from Polysciences Inc.

PVA and PVP were dissolved in distilled water at a concentration of 3 wt% separately. The two solutions were mixed together at room temperature at the compositions listed in *Table 1*. After stirring the mixed solutions for 2.5 h, the solvent water was allowed to evaporate at room temperature for several days. Transparent films were obtained. These PVA/PVP blend films were finally dried under reduced pressure at a temperature of 333 K for 5 days. Pure PVA and PVP samples were also prepared in the same manner.

### *N.m.r. experiments*

N.m.r. experiments were carried out on a JEOL JNM-GX270 spectrometer operating at frequencies of 270 and 67.8 MHz for $^1H$ and $^{13}C$, respectively. High-resolution solid-state $^{13}C$ n.m.r. was realized by applying magic-angle sample spinning (MAS) and high-power spin decoupling. To enhance the signal-to-noise ratio, the cross-polarization (CP) technique was applied. The $^1H$ decoupling frequency was chosen at 3 ppm downfield from tetramethylsilane (TMS). A double-bearing aluminium oxide rotor was used. The setting of the magic angle was monitored by the $^{79}Br$ n.m.r. spectrum of KBr incorporated in the rotor[18]. The radiofrequency field strength for both $^1H$ and $^{13}C$ was about 56 kHz. $^{13}C$ CP/MAS spectra were measured with the normal CP/MAS pulse sequence of a contact time of 1 ms and a magic-angle spinning rate of about 6 kHz. In order to examine the cross-polarization process of the blends, the contact time was varied from 10 $\mu$s to 5 ms. Measurements of $^1H$ $T_{1\rho}$ and $T_1$ were made by methods reported elsewhere[10,19]. The chemical shift of $^{13}C$ spectra were reported in parts per million (ppm) relative to TMS by taking the methine carbon resonance of solid adamantane (29.5 ppm) as an external reference standard. The variable-temperature control was accomplished using a JEOL MVT temperature controller. The temperature of the samples was calibrated by the conventional methanol method[20].

## RESULTS AND DISCUSSION

### *$^{13}C$ CP/MAS spectra of PVA/PVP blends*

The $^{13}C$ CP/MAS spectra of PVA, PVP and PVA/PVP blends in 81/19, 30/70 and 17/83 weight ratios (wt%) at a temperature of 311 K are shown in *Figure 1*. The assignment of the spectra of PVA and PVP was made by reference to previous results[21,22]. The three-peak characteristic of the CHOH carbon of PVA is attributed to intramolecular hydrogen bonding in the solid state. Terao *et al.* assigned peak 'a' to an *mm* triad that is hydrogen-bonded to both the two nearest neighbours, peak 'b' to *mm* and *mr* triads that are hydrogen-bonded to one of the nearest neighbours and peak 'c' to *mm*, *mr* and *rr* triads that are not hydrogen-bonded[21] (see *Figure 1A*). The degree of intramolecular hydrogen bonding of PVA can be monitored through the intensity of peaks 'a' and 'b'.

A comparison of the $^{13}C$ CP/MAS spectra of PVA/PVP blends with those of pure PVA and PVP shows an alteration of isotropic chemical shift with composition. The carbonyl carbon resonance of PVP component in the blends shifts downfield with increasing PVA composition, as seen in *Figure 2*. The chemical shift ranges from 175.5 ppm for pure PVP to 177.7 ppm for PVA/PVP = 56/44 blend, and does not change with further increase of PVA composition.

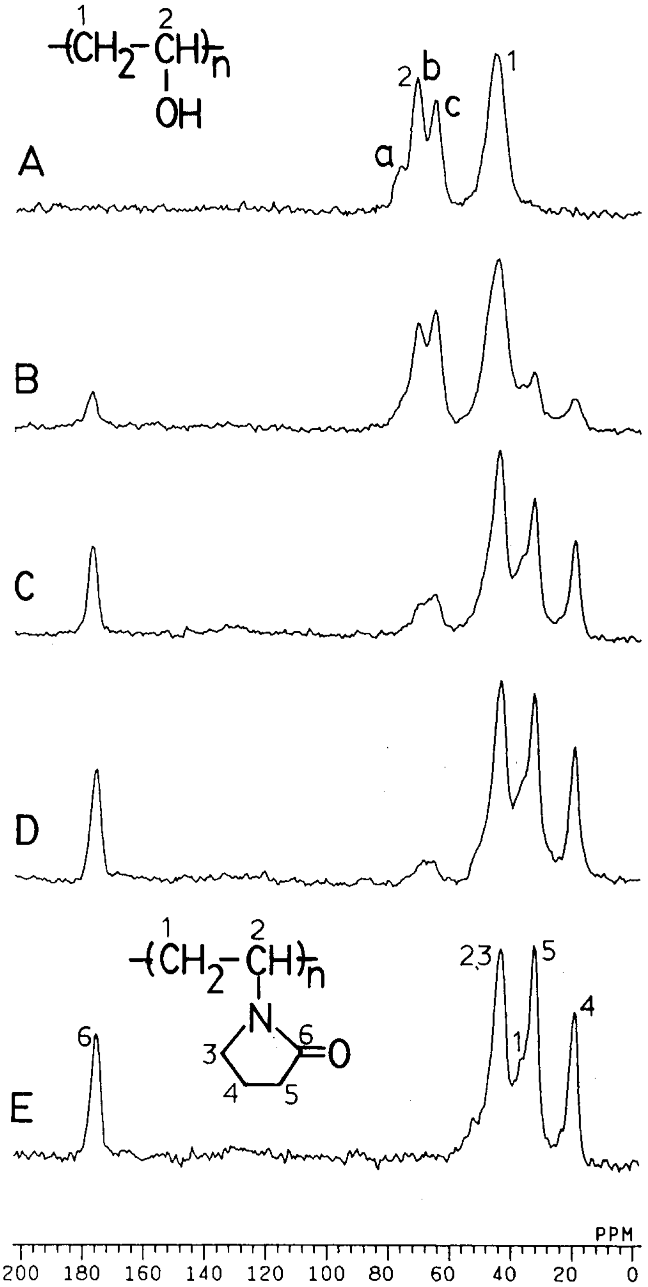

Figure 1 $^{13}C$ CP/MAS n.m.r. spectra of PVA, PVP and PVA/PVP blends at 311 K: (A) pure PVA; (B) PVA/PVP = 81/19, (C) PVA/PVP = 30/70, (D) PVA/PVP = 17/83 blends; (E) pure PVP. Peak assignments of PVA and PVP are also displayed

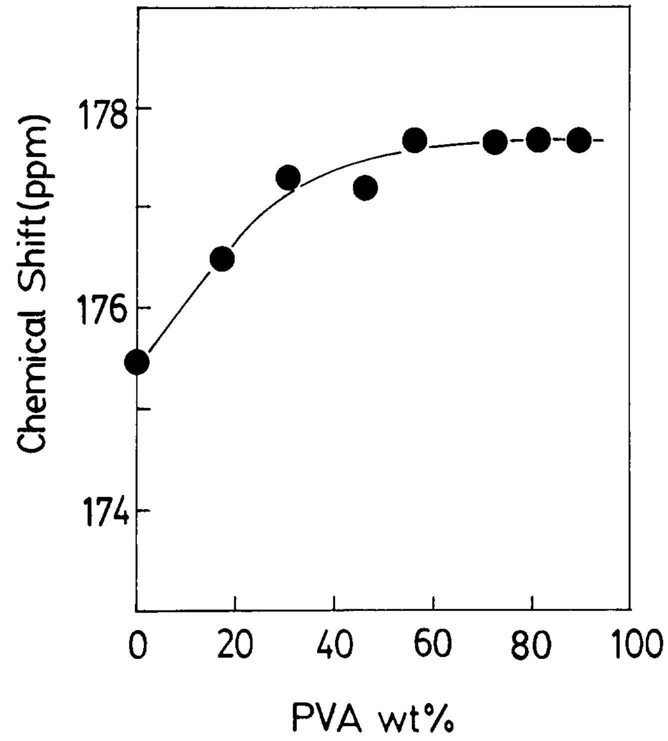

**Figure 2** The chemical shift of the carboxyl carbon resonance of PVP component in PVA/PVP blends as a function of the PVA composition

The carbonyl carbon resonance of PVP would be expected to shift downfield if hydrogen-bonded, since it resonates at 172.9 ppm in the non- or weak hydrogen-bonded state in chloroform solution and at 178.8 ppm in the strong hydrogen-bonded state in aqueous solution[22]. Thus, the observed downfield shift of the carbonyl carbon resonance of PVP in the blends is probably attributed to a hydrogen-bonding interaction between PVA and PVP. When the PVA composition is less than the equimolar ratio to PVP, the excess amount of PVP cannot find counterparts with which to form intermolecular hydrogen bonds. Thus, it resonates at its original position. The observed resonance of the carbonyl carbon is the weighted average of the two peaks of hydrogen-bonded and non-hydrogen-bonded groups. Because the difference in chemical shift of the two peaks is smaller than the linewidth, the two peaks appear as a single line at a weighted average chemical shift position. When the molar ratio of PVA is more than the PVP composition, the amount of hydrogen-bonded PVP is saturated, and the chemical shift levels off.

The spectral pattern of the three-peak CHOH carbon of PVA also shows a noticeable alteration as the composition of PVA decreases (*Figure 3*). With decreasing PVA composition in the blends, peak 'a' of CHOH resonance decreases in intensity while peak 'c' increases. Peak 'b' decreases in intensity upon the initial addition of PVP, and remains unchanged upon further addition of PVP composition.

A similar change in the three-peak characteristic of the CHOH resonance of PVA was reported for poly(vinyl alcohol)/poly(acrylic acid) blends[1]. The decrease in intensity of peaks 'a' and 'b' of the CHOH resonance of PVA can be attributed to the dissociation of intramolecular hydrogen bonds between the two nearest neighbours of hydroxyl groups in PVA and the formation of an intermolecular hydrogen bond between PVA and PVP. Since the formation of an intermolecular hydrogen bond is independent of the tacticity, the spectra would lose the three-peak characteristic. Such spectral change provides further evidence for intermolecular hydrogen bonding between the carbonyl group of PVP and the hydroxyl group of PVA.

*Intermolecular cross-polarization of PVA/PVP blends*

The cross-polarization process is a process of magnetization transfer from proton to carbon during the cross-polarization contact time. Therefore, the cross-polarization process strongly depends on the proton–carbon distance. The contact time dependence of the intensity of carbon resonances was measured for pure PVA, pure PVP and PVA/PVP blends (*Figure 4*). It appears that the cross-polarization process consists of two processes for CH$_2$ and CHOH carbon resonances of PVA. The fast process is attributed to the dipolar interaction between carbon and protons directly bonded to it and the slow one to spin diffusion. Even a short contact time of 0.5 ms is enough to achieve full enhancement. The situation was similar for protonated carbons of PVP (the results are not shown). For the carbonyl carbon of PVP, the enhancement occurs much more slowly because no proton is directly bonded to it. It is of interest to note that the carbonyl carbon resonance of PVP in the blends increases in intensity faster than that of pure PVP. These results indicate that intermolecular cross-polarization between the protons of PVA and the carbonyl carbon of PVP does occur in the blends. This would be possible if the average distance between the carbonyl carbon of PVP and the protons of PVA is less than 10 Å; an appreciable dipole–dipole coupling between the protons of PVA and the carbonyl carbon of PVP is effectuated, which causes a faster enhancement[10,16,17]. The hydroxyl proton of PVA, which has close contact

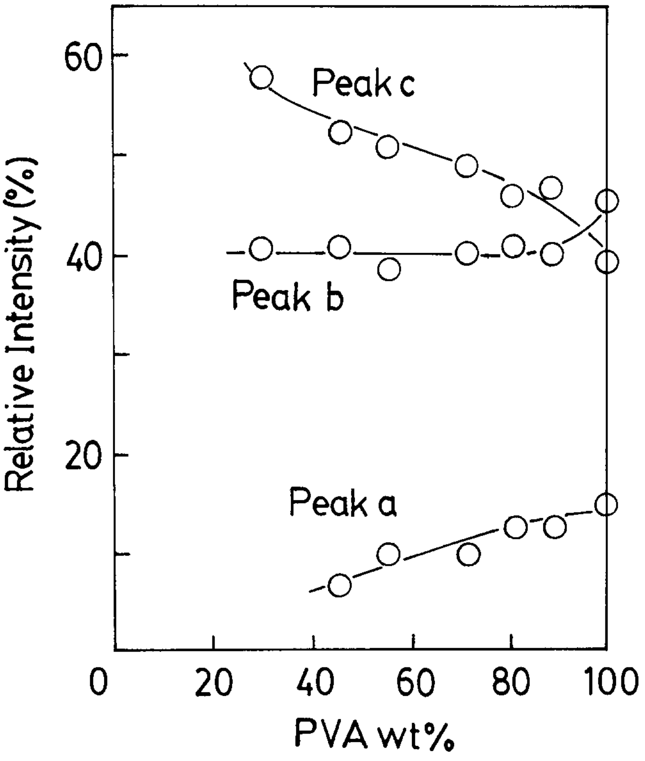

**Figure 3** The PVA composition dependence of the intensity of the CHOH carbon resonance of PVA component in PVA/PVP blends

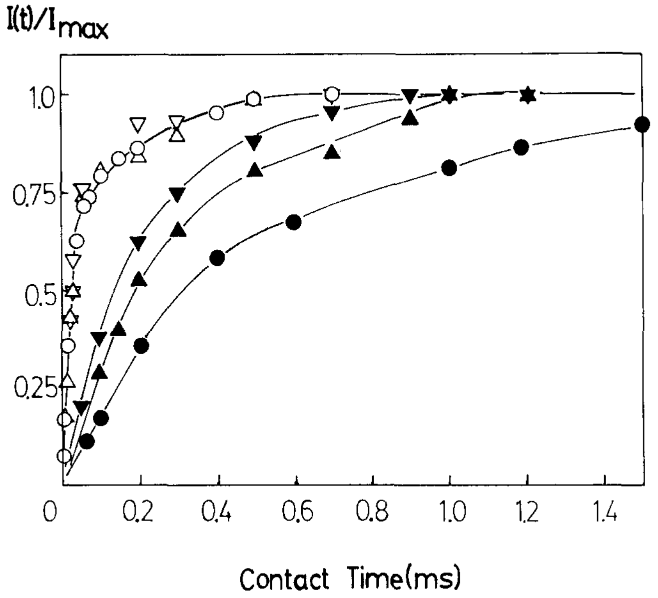

**Figure 4** The relative intensity as a function of $^1$H/$^{13}$C cross-polarization contact time for the carbonyl carbon resonance of PVP in pure PVP (●), PVA/PVP = 30/70 (▲) and PVA/PVP = 72/28 (▼), and for the CHOH carbon resonance of PVA in pure PVA (○), PVA/PVP = 30/70 (△) and PVA/PVP = 72/28 (▽)

**Table 2** $^1$H $T_{1\rho}$ values of PVA/PVP blends at 311 K[a]

| | CO | CHOH |
|---|---|---|
| PVA | | 3.5 (43%), 9.6 (57%) |
| PVA/PVP = 89/11 | 3.4 | 3.3 (72%), 9.5 (28%) |
| PVA/PVP = 81/19 | 3.3 | 3.1 (77%), 11 (23%) |
| PVA/PVP = 72/28 | 3.6 | 3.5 (82%), 9.9 (18%) |
| PVA/PVP = 56/44 | 4.0 | 4.9 |
| PVA/PVP = 46/54 | 4.4 | 4.4 |
| PVA/PVP = 17/83 | 6.3 | 6.3 |
| PVP | 19 | |

[a] Values are expressed in milliseconds, PVA and PVA/PVP = 89/11, 81/19, 72/28 blends show two components for PVA component. The value in parentheses shows percentage of the two components in proton number

with the carbonyl oxygen of PVP through hydrogen bonding, can be considered as a source of the $^1$H/$^{13}$C magnetization transfer. These results also suggest that in blends the two polymers are mixed intimately on the molecular level, or at least the blends consist of miscible domains. Such intermolecular cross-polarization effects have also been reported for other miscible blends, for example, poly(methyl methacrylate)/poly(vinylidene fluoride)[17] and polystyrene/poly(vinyl methyl ether) blends[23].

### $^1$*H* $T_{1\rho}$ *and* $T_1$ *of PVA/PVP blends*

Since the alteration of domain structure would reflect on relaxation behaviour, the domain structure can be studied by observing the n.m.r. relaxation parameter. If two different polymers are intimately mixed, the relaxation times of different protons would be equalized by spin diffusion. This is also the case if the domain size of heterogeneous systems is smaller than the maximum path length of spin diffusion, which depends on the method of relaxation measurement. Typically, $^1$H $T_{1\rho}$ provides information about domain structure on a scale of 20–30 Å, and $^1$H $T_1$ on a scale of 200–300 Å[24–26]. $^1$H $T_{1\rho}$ values of PVA, PVP and PVA/PVP blends at a temperature of 311 K measured through $^{13}$C resonance of CO and CHOH by the CP/MAS technique are listed in *Table 2*.

All $^{13}$C resonances of the pure PVP sample show an identical single-exponential decay in the $^1$H $T_{1\rho}$ experiment, indicating that fast spin diffusion among protons equalizes relaxations of all protons. On the other hand, $^1$H $T_{1\rho}$ decay for pure PVA is non-exponential. It can be decomposed into two components: the slower relaxation component is assigned to the crystalline phase, and the faster one to the intermediate phase[1]. The amorphous phase would not be observed in the present experiment, because it has weak CP ability[21]. $^1$H $T_{1\rho}$ of the amorphous phase would be shorter than that of the intermediate phase since molecular motion in the amorphous phase is expected to be faster than that in the intermediate phase. In *Table 2*, the percentages of the two components of PVA are also listed. Owing to the difference in CP ability of each phase, the percentage (intensity ratio) does not express the real composition of each phase. The percentage only expresses approximately the ratio of crystalline and intermediate phases.

For PVA/PVP blends at all compositions, the $^1$H $T_{1\rho}$ decay of PVP component (observed by the carbonyl carbon resonance) is single-exponential; it becomes much faster with increasing PVA composition. The $^1$H $T_{1\rho}$ decay of PVA component in the blends at PVA compositions less than 56 wt% appears single-exponential. For the PVA/PVP = 17/83, 30/70 and 46/54 blends, the $T_{1\rho}$ values of PVA and PVP components are identical at 311 K. For the PVA/PVP = 56/44 blend, the $T_{1\rho}$ value of PVA component is somewhat larger than that of PVP component. For the blends at PVA compositions higher than 72 wt%, the $^1$H $T_{1\rho}$ decay of PVA component seems to be two-exponential. The two $T_{1\rho}$ values are quite similar to those of pure PVA, but the apparent percentage of the longer $T_{1\rho}$ component for the blends is much less than that of pure PVA (57%) in number of protons. As the PVA composition decreases, the amount of the longer $T_{1\rho}$ component decreases further, and becomes only about 18% when the PVA/PVP composition reaches 72/28 (*Table 2*).

On the other hand, for the PVA/PVP = 17/83 blend, which has the highest PVP composition in the present

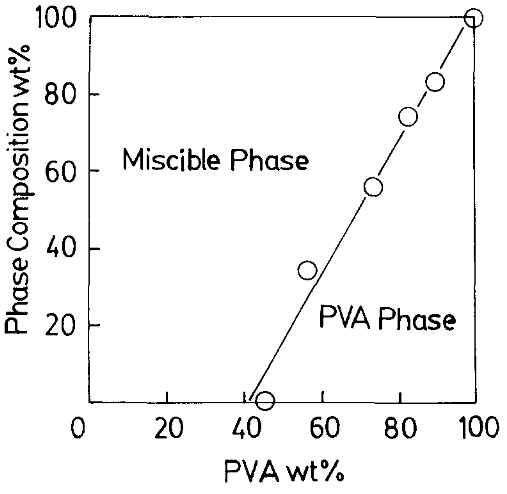

**Figure 5** The phase composition of the blends at 311 K as a function of the PVA composition

**Table 3** $^1$H $T_1$ values of PVA/PVP blends at 311 K[a]

| | CO | CHOH |
|---|---|---|
| PVA | | 7.3 |
| PVA/PVP = 89/11 | 2.7 | 3.4 |
| PVA/PVP = 81/19 | 4.2 | 4.0 |
| PVA/PVP = 72/28 | 3.2 | 3.5 |
| PVA/PVP = 56/44 | 3.5 | 3.8 |
| PVA/PVP = 46/54 | 3.4 | 3.5 |
| PVA/PVP = 17/83 | 2.2 | 2.3 |
| PVP | 2.0 | |

[a] Values are expressed in seconds

work, no $^1$H $T_{1\rho}$ component corresponding to pure PVP phase (with the value of 19 ms) can be observed from the carbonyl carbon resonance.

These results indicate that, when the PVA composition is less than 46 wt%, the two polymers are mixed so intimately that the blends are homogeneous. Strong dipole–dipole interactions occur between PVA and PVP. No detectable domains can be observed on a scale of 20–30 Å. When the PVA composition is more than 72 wt%, the miscibility is poor. Only a partial amount of PVA in the blends is mixed with PVP to form a miscible phase, while the excess PVA forms a pure PVA phase, and still retains a domain structure similar to pure PVA on a scale larger than 20–30 Å. For the PVA/PVP = 56/44 (3/1 molar ratio) blend in which the crystallinity of PVA phase is small, the $T_{1\rho}$ decay may be erroneously analysed as single-exponential though in reality it is two-exponential. Thus, we have a longer $T_{1\rho}$ value of 4.9 ms for the PVA component. However, even for PVA-rich blends, the effect of blending is noticeable. The crystalline phase of PVA is destroyed significantly by the introduction of an increasing amount of PVP. When the PVA composition is less than 56 wt%, the amount of crystalline phase of PVA becomes too small to be observed. Such reduction in crystallinity of PVA is well known for miscible blends of crystalline polymer/amorphous polymer, for example, poly(vinylidene fluoride)/poly(methyl methacrylate)[13], poly(vinylidene fluoride)/poly(ethyl methacrylate)[27] and poly(phenyl sulphide)/polystyrene blends[28].

To summarize, on the scale of 20–30 Å, the blends with PVA composition more than 46 wt% comprise two phases: one is the amorphous miscible phase consisting of PVA plus PVP, and the other is the pure PVA phase in which the crystallinity is much reduced. When the PVA composition is less than 46 wt%, the two polymers are mixed intimately. No detectable domain structure can be found on a scale of 20–30 Å. There is no pure PVP phase even in the PVP richest blend.

Under the assumption of strong spin-diffusion coupling, the average relaxation time of a two-component system can be given as[24,26]:

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

where $T_{1\rho}(1)$ and $T_{1\rho}(2)$ denote the observed relaxation times of pure components 1 and 2, respectively; $N_1$ and $N_2$ are the numbers of protons in the respective components; and $N$ is the total number of protons in the system, $N = N_1 + N_2$. For homogeneous blends at PVA compositions less than 46 wt%, we simply assume that the observed $T_{1\rho}$ value (measured from the carbonyl carbon resonance) is an average of those of pure PVP ($T_{1\rho}(1) = 19$ ms) and amorphous PVA component (unknown $T_{1\rho}(2)$). Observed $^1$H $T_{1\rho}$ values for PVA/PVP = 17/83 and 30/70 blends give an estimated $T_{1\rho}(2)$ value for amorphous PVA of 1.6 ms, which is smaller than the value of the intermediate phase, 3.5 ms.

Using $T_{1\rho}(1) = 19$ ms, $T_{1\rho}(2) = 1.6$ ms and $N_1/N$ corresponding to the composition of PVP, the composition of amorphous PVA in the miscible phase in blends at PVA compositions more than 46 wt% can be determined from equation (1). The composition of pure PVA phase in the blends thus inferred is depicted as a function of PVA composition in *Figure 5*. In the above estimation, we assumed that the motional state is not affected by blending. Also we do not take into account the existence of an interface between the two phases.

To explore the miscibility of the blends on a somewhat larger scale, $^1$H $T_{1\rho}$ of PVA/PVP blends was measured at 311 K. The results are listed in *Table 3*. Single $T_1$ values for two pure polymers and the blends were observed, suggesting that the two polymers are miscible on a scale of 200–300 Å. A single $T_1$ value has also been reported for poly(vinyl alcohol)/poly(acrylic acid)[1].

## CONCLUSIONS

Although a single glass transition has been reported for PVA/PVP blends at all compositions, the present $^{13}$C CP/MAS n.m.r. results indicate that, when the PVA composition is more than 46 wt%, the blends comprise the amorphous miscible phase of PVP plus PVA and the pure PVA phase on a scale of 20–30 Å. The crystalline phase of PVA component in the blends decreases remarkably with decreasing PVA composition. When the PVA composition is less than 46 wt%, the blends are miscible on a scale of 20–30 Å, and the crystalline phase of PVA disappears completely. All blends are homogeneous on a scale of 200–300 Å. The miscibility is caused by the intermolecular hydrogen-bonding interaction between the carbonyl group of PVP and the hydroxyl proton of PVA, as evidenced by both the downfield shift of the carbonyl carbon resonance of PVP and the change in spectral lineshape of the CHOH carbon of PVA in the blends. The intermolecular cross-polarization provides additional evidence for hydrogen bonding and intimate mixing of the blends.

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