

Thermal and spectroscopic properties of zinc perchlorate/poly(vinylpyrrolidone) blends and a comparison with related hydrogen bonding systems

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Abstract

We have investigated the thermal and spectroscopic properties of blends of poly(vinylpyrrolidone) (PVP) with zinc perchlorate. Analyses by differential scanning calorimetry indicates that blending with zinc perchlorate increases the values of T_g of PVP. We calculated the interaction strength of the zinc salt/PVP blends based on an extended configuration entropy model. The presence of ion–dipole interactions between PVP and the zinc salt was confirmed based on Fourier transform infrared (FTIR) and solid-state NMR spectroscopies, which suggest that the zinc cations coordinate with the carbonyl groups of PVP. The single value of T_p^H measured by solid-state NMR spectroscopy observed for all the zinc salt/PVP blends is smaller than that of pure PVP, which is a finding that indicates that the domain size of this blend system decreases upon increasing the zinc salt content. Based on FTIR and solid-state NMR spectroscopic analyses, we conclude that the ion–dipole interactions in the zinc salt/PVP blend are stronger than the hydrogen bonds in systems such as the poly(vinylphenol) (PVPh)/PVP blend and the PVPh-*co*-PVP copolymer.

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1. Introduction

Polymer blending is a convenient and attractive route for obtaining new polymeric materials that have desirable combination of physical properties. Most polymers pairs, however, are immiscible because the high degree of polymerization of polymers results in a vanishingly small entropy term for the free energy of blending. To enhance the formation of one single-phase system in polymer blends, it is necessary to ensure that specific interactions, such as ionic, hydrogen bonding, and dipole–dipole interactions, exist between the two components. Recently, polymer blending with inorganic salts has become an interesting method for producing new materials with better thermal, mechanical, and conductivity properties, as well as for

materials that can separate olefin/paraffin gas mixtures [1–4].

Increasing both the intermolecular cohesion and glass transition temperatures of polymers is a subject of long-standing interest. Polymers possessing higher glass transition temperatures are attractive in polymer science as a result of the strong economic incentives that arise from their potential applications. In a previous study [5], we found that the values of T_g of PVPh/PVP blends are higher than their mother polymers. Furthermore, based on DSC and Fourier transform infrared (FTIR) and solid-state NMR spectroscopic analyses, the values of T_g and the hydrogen bonding strengths of PVPh-*co*-PVP copolymers are greater than those of their corresponding PVPh/PVP blends at the same mole fractions of PVPh [6,7]. In addition, the values of T_g of PVPh-*co*-PVP-*co*-POSS nanocomposites are increased dramatically in comparison with the corresponding PVPh-*co*-PVP copolymers because of the strong hydrogen bonding that exists in this system [8]. PVP is amorphous and possesses a high value of T_g because of its rigid pyrrolidone

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group, which is capable of forming a variety of complexes with many inorganic salts [9–11]. The variations of T_g with respect to the zinc salt concentration are of special interest to researchers studying polymer electrolytes. The incorporation of zinc salts into a PVP matrix causes the polymer chains to rigidify as a result of the physical cross-linking that occurs between the PVP chains and the metal atoms; this process results in the value of T_g increasing. In this study, therefore, we have investigated, by DSC and FTIR and solid-state NMR spectroscopic analyses, the mechanism by which the enhancement of the values of T_g of PVP occurs upon blending it with zinc perchlorate and provide a comparison of this system with regard to related hydrogen bonding systems.

Solid-state NMR and FTIR spectroscopies are powerful tools for characterizing the structural details of polymer interactions because these specific interactions affect the local electron density and, consequently, corresponding frequency shifts can be observed [12–15]. Moreover, solid-state NMR spectroscopy can be used to measure the phase behavior and the morphology of polymer blends, which can be estimated from the proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^H$). In this paper, we report the complex interactions that exist between PVP and zinc perchlorate, and provide direct evidence to support the nature of the proposed ionic interactions.

2. Experimental

2.1. Materials

Poly(vinylpyrrolidone) (PVP) having $M_n = 58,000$ g/mol was obtained from the Acros Chemical Company. Zinc perchlorate hexahydrate [$Zn(ClO_4)_2 \cdot 6H_2O$], obtained from Aldrich, was dried in a vacuum oven at 70 °C for 24 h. *N,N*-Dimethylformamide (DMF) was used as received.

2.2. Preparation of polymer–salt mixtures

Zinc salt/PVP blends having varying zinc content were prepared by dissolving the desired amounts of the polymer and $Zn(ClO_4)_2 \cdot 6H_2O$ in DMF. After stirring continuously for 12 h, these solutions were maintained at 50 °C for 24 h on Teflon plates to facilitate desolvation, and then dried further under vacuum at 90 °C for 2 days.

2.3. Characterization

Thermal properties were measured using a TA Instrument DSC 2010. The measurements were conducted under a nitrogen flow rate of ca. 25 ml/min. All samples were heated to 300 °C, subsequently annealed for 3 min, rapidly cooled to 20 °C, and then reheated. A heating rate of 20 °C/min was used in all cases. The glass transition temperature (T_g) was taken as the midpoint of the transition. All IR spectra were

recorded in the range 4000–400 cm^{-1} at a spectral resolution of 1 cm^{-1} after 32 scans using a Nicolet Avatar 320 FTIR spectrophotometer. IR spectra of mixture films were measured using the conventional KBr disk method: a DMF solution of the mixture was cast onto a KBr disk and the solvent was evaporated at 90 °C for 24 h. IR spectra were obtained at 120 °C by using a cell mounted inside the temperature-controlled compartment of the spectrometer. The film used in this study was sufficiently thin to obey the Beer–Lambert law. High-resolution solid-state ^{13}C NMR spectroscopy experiments were carried out at room temperature using a Bruker DSX-400 spectrometer operating at resonance frequencies of 399.53 and 100.47 MHz for 1H and ^{13}C nuclei, respectively. The ^{13}C CP/MAS spectra were measured using a 3.9 μs 90° pulse, a 3 s pulse delay time, and an acquisition time of 30 ms, with a total of 2048 scans. All NMR spectra were recorded at 25 °C using broadband proton decoupling and a normal cross-polarization pulse sequence. A magic-angle sample-spinning (MAS) rate of 5.4 kHz was used to avoid absorption overlapping. The proton spin–lattice relaxation time in the rotating frame ($T_{1\rho}^H$) was determined indirectly by observing carbon nuclei using a 90°- τ -spin-lock pulse sequence prior to cross polarization. The data acquisition was performed by 1H decoupling with delay times (τ) ranging from 0.1 to 12 ms and a contact time of 1.0 ms.

3. Results and discussion

3.1. Analyzing thermal properties

Fig. 1 shows DSC analyses of zinc salt/PVP blends having various compositions. Clearly, the value of T_g increases as the zinc salt concentration increases, with the maximum enhancement of T_g being ca. 47 °C for PVP containing 40 wt% of the zinc salt, and then the values of T_g decrease at higher zinc salt concentration. Recently, Kim et al. proposed [16] an extended configuration entropy model to predict the behavior of T_g of complexing polymer–salt systems:

$$\ln \frac{T_{g12}}{T_{g1}} = \beta \left[\left(1 - \gamma_{12} \ln \left(\frac{z-1}{e} \right) \right) \left(\frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right) - \frac{\phi_2}{r_2} \frac{4}{3} A_{\text{diss}} I_{3/2} \tau (I^{1/2}) \right] \quad (1)$$

where T_{g1} and T_{g12} are the glass transition temperatures of the pure polymer and of the polymer–salt blend, respectively, and ϕ_i and r_i are the volume fraction and the degree of polymerization, respectively, for component *i*. Here, $r_2 = 1$ and $\beta = zR/M_{1u}\Delta C_{pp}$, where z (= 12) is the lattice coordination number, R is the gas constant, M_{1u} is the molecular weight of the repeating unit of the polymer, and

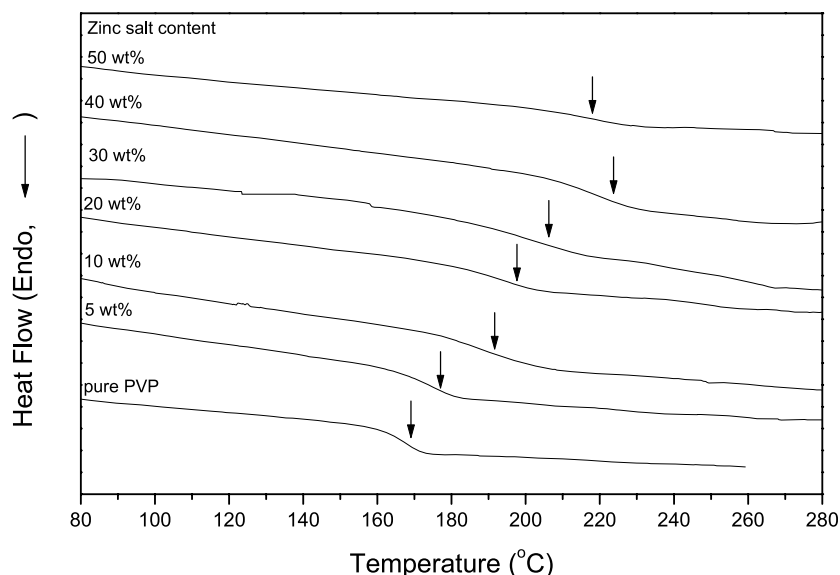


Fig. 1. DSC scans of zinc salt/PVP blends having a variety of compositions.

ΔC_{pp} is the isobaric specific heat of polymer. The proportionality constant r_{12} represents the strength of the interaction between the polymer and salt. The equation $(\phi_2/r_2vm)(4/3)A_{diss}I_{3/2}\tau(I^{1/2}) = A^{DH}$ is extended to account for the cation–anion interaction. Table 1 lists the molecular weight, T_g , specific heat, and density of the components used in this study. It is well known that the presence of the zinc salt leads to retardation of chain mobility, which results in higher values of T_g . Polymer–cation interactions occur commonly in metal salt/polymer blend system, but an excessive metal salt content tends to decrease the value of the polymer's T_g because the interchain distance increases and micro-phase separation occurs above a certain optimized concentration [17]. Fig. 2 shows the variation in T_g as a function of zinc salt content; the solid lines, calculated using Eq. (1), imply that good correlations exist between the experimental data and model's predictions. The interaction parameters of the zinc salt/PVP blend ($r_{12} = 1.50$, $A^{DH} = 0.06$) are lower than those of the zinc salt/poly(4-vinylpyridine) blend system ($r_{12} = 3.60$, $A^{DH} = 0.06$) [18]. This result is consistent with the findings of a previous study in which the ionic interactions in the poly(vinylpyridine) blend system were determined to be greater than those in the PVP blend system [19].

3.2. Infrared spectroscopic analyses

The most frequently employed method for quantifying the relative fraction of free and bonded carbonyl sites within a PVP polymer chain is to measure the extent of such interactions by monitoring the carbonyl stretching bands in the IR spectra as a function of the blend composition. Fig. 3 shows the carbonyl stretching region, in the range 1520–1760 cm^{-1} , of the IR spectra of zinc salt/PVP blends recorded at 120 °C. The stretching band of the free carbonyl group of uncomplexed PVP appears at 1680 cm^{-1} . This band broadens gradually as the zinc salt content increases and a new band, at ca. 1615 cm^{-1} , appears and grows. This new band corresponds to the coordination interaction between the zinc ion and the carbonyl oxygen atom. The fraction of the complexed carbonyl groups can be measured at different zinc salt ratios by decomposing the carbonyl stretching region into two Gaussian peaks, as is shown in Fig. 4. Table 2 summarizes results from curve fitting of these peaks; we observe that the fraction of complexed carbonyl groups increases upon increasing the zinc salt content. These results suggest that $\text{Zn}(\text{ClO}_4)_2$ dissociates into the PVP matrix through the coordination of zinc ions with carbonyl oxygen atoms and that one zinc cation binds to each carbonyl oxygen atom of PVP.

Table 1
Molecular weights, values of T_g , specific heats, and densities of the components used in this study

	M_w (g/mol)	T_g (°C)	ΔC_{pp} (J/(kg K) ^a	Density (g/cm ³)
PVP	58,000	173	2080	1.563
$\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$	372	–	–	2.052 ^b
Blend system	z	β	r_{12}	A^{DH}
PVP/ $\text{Zn}(\text{ClO}_4)_2$	12	0.6809	1.5	0.06

^a Values obtained from the group contribution method [22].

^b Value obtained from the density measurement [18].

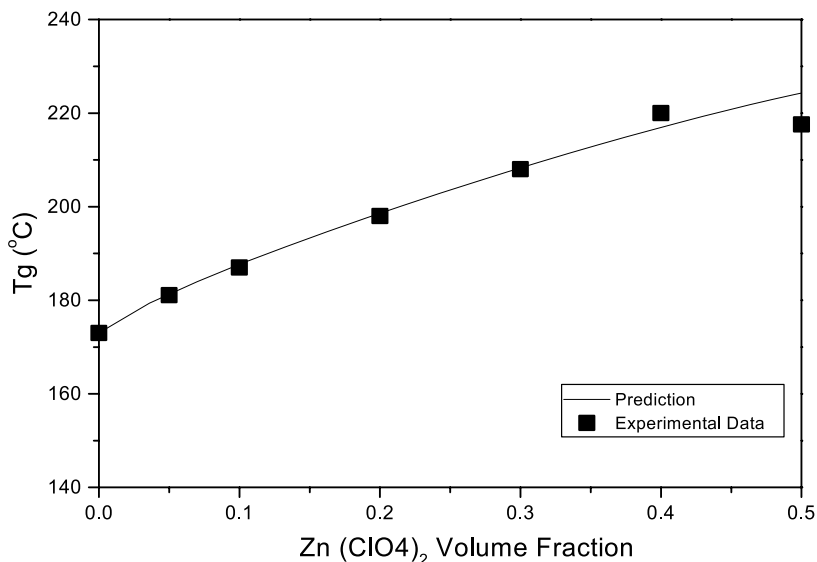


Fig. 2. Variations in the values of T_g of PVP blended with the zinc perchlorate; the solid lines are values calculated from the configuration entropy model.

The change in the relative intensity and the location of the ClO_4^- anion within the complex depend on the concentration of the $\text{Zn}(\text{ClO}_4)_2$ salt; consequently, these changes can be attributed to interactions involving the ClO_4^- . Fig. 5 shows IR spectra of pure PVP and various zinc salt/PVP complexes, presenting the ClO_4^- stretching bands in the

range from 650 to 600 cm^{-1} , recorded at $120\text{ }^\circ\text{C}$. Within this region, the absorptions at 627 and 635 cm^{-1} , which represent $\nu(\text{ClO}_4^-)$ vibrations, correspond to free and contact ions, respectively [20]. When the zinc salt concentration is increased, the contact ion band shifts to higher frequency and the band becomes asymmetric. The asymmetric shape of the band may be attributed to the existence of both free ions and ion pairs. Fig. 5 also shows the deconstruction of the bands of ClO_4^- anion of the pure zinc salt into two Gaussian peaks. Table 3 summarizes results from curve fitting and indicates that the fraction of ClO_4^- anions existing in ion pairs increases as the zinc salt content increases; this finding can be interpreted as the ClO_4^- anion interacting gradually with zinc cation to facilitate the cation–anion interaction with increasing zinc salt concentration.

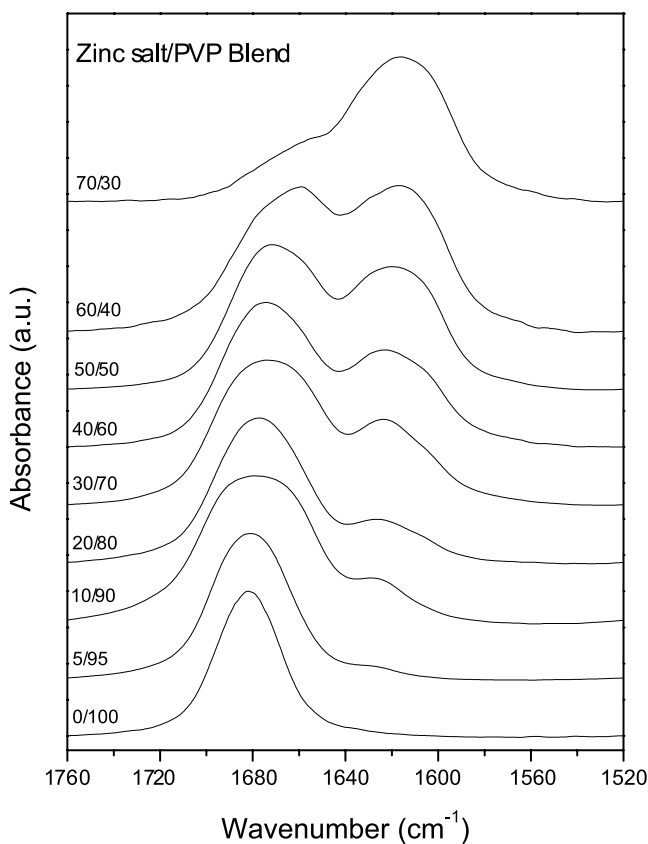


Fig. 3. FTIR spectra, presenting the region 1760 – 1520 cm^{-1} , of weight fraction of the zinc salt/PVP blends recorded at $120\text{ }^\circ\text{C}$.

3.3. Analyses by solid state NMR spectroscopy

Solid-state NMR spectroscopy provides further insight into the interaction behavior, phase behavior, and morphology of the polymer blends formed from PVP and the zinc salt. Upon coordination, the coordinating units experience small perturbations in the magnetic shielding of their nuclei, which results in downfield chemical shifts of their corresponding carbon atoms relative to those of the free polymers. Figure 6 shows the ^{13}C CP/MAS NMR spectra of pure PVP and its blends with zinc perchlorate; Scheme 1 indicates the atom numbering used to assign these peaks. The spectrum of pure PVP exhibits peaks for six major resonances. Table 4 summarizes the values of the chemical shifts observed in the ^{13}C CP/MAS NMR spectra of the zinc salt/PVP blends. Compared with the ^{13}C CP/MAS NMR spectra of the pure polymers, the spectra of the zinc salt/PVP blends display significant changes, especially for the resonances of the carbon atoms involved in intermolecular ion–dipole interactions. For example, the

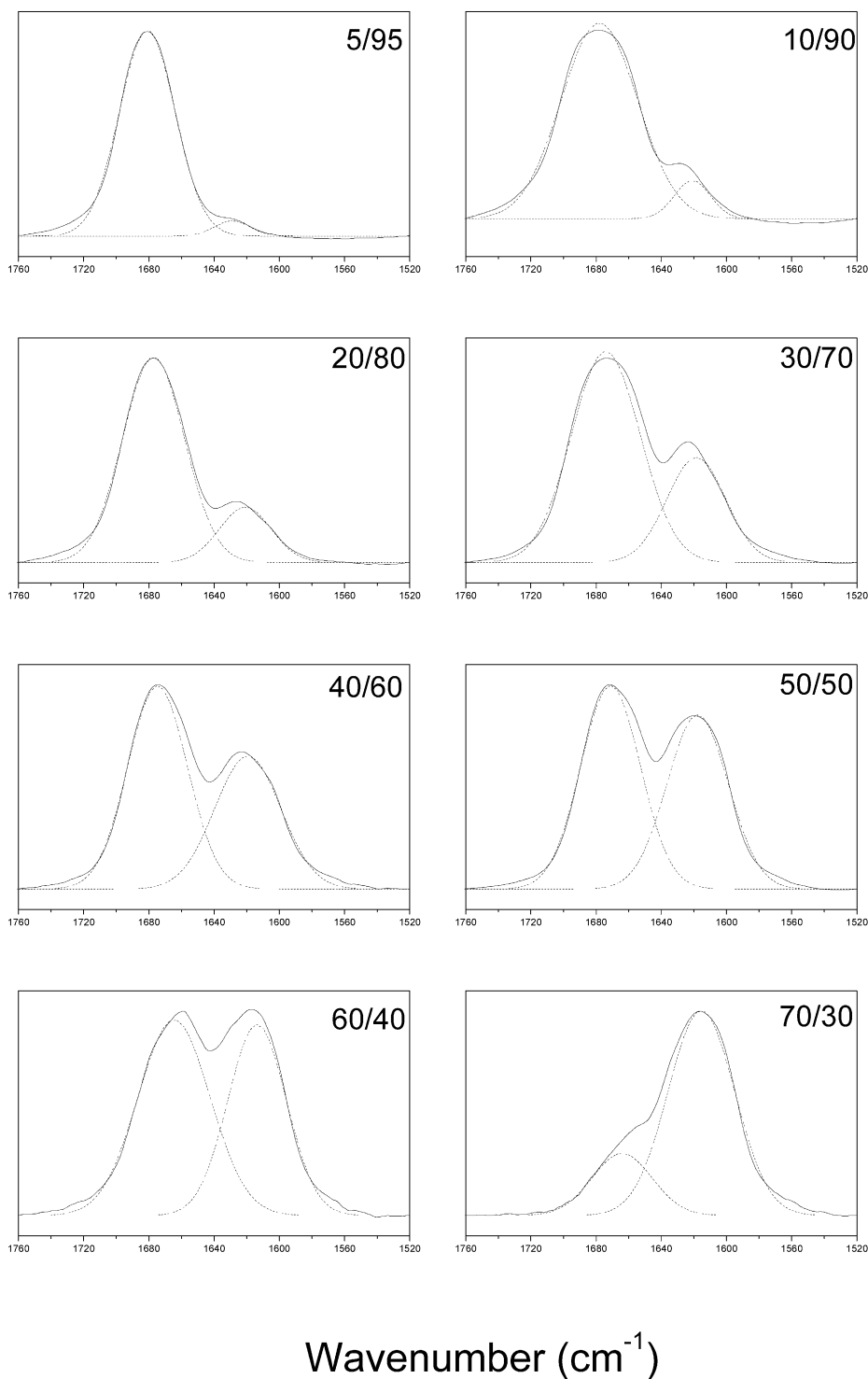


Fig. 4. Deconstructed models of the carbonyl stretching bands (in Fig. 3) of the weight fraction of zinc salt/PVP blends at various zinc salt concentrations.

carbonyl resonance of PVP is shifted downfield by ca. 2 ppm at a zinc salt content of 40 wt%. It is well known that intermolecular interactions in polymer blends can affect the chemical environments of the interacting molecules, which can result in relatively downfield chemical shift. The signals of the C2, C4, and C5 atoms, as well as the carbonyl group's resonance (C-6), shift downfield upon increasing the zinc

salt concentration, as indicated in Table 4. These carbon atoms display the character of being positioned adjacent to electron donating units: the C4 and C5 atoms are adjacent to N atoms and the C2 atom is near the carbonyl group. The strong electron withdrawing character of the N atom and carbonyl is able to function as a quasi-cation within the PVP chain to attract the anion that result in down-filed shift. In

Table 2
Curve fitting of the area fractions of the carbonyl stretching bands in the FTIR spectra of zinc salt/PVP blends recorded at 120 °C

Zn salt/PVP wt ratio	Free C=O		Ionic interaction C=O		f_i
	ν (cm^{-1})	A_f (%)	ν (cm^{-1})	A_i (%)	
0/100	1682	100	—	—	0
5/95	1681	95.5	1629	4.5	3.5
10/90	1678	91.6	1621	8.4	6.6
20/80	1677	81.5	1620	18.5	14.8
30/70	1674	70.2	1619	29.8	24.6
40/60	1674	57.9	1618	42.1	35.9
50/50	1671	53.2	1617	46.8	40.4
60/40	1665	44.2	1614	55.8	49.3
70/30	1664	21.5	1614	78.5	73.8

ν , wavenumber; $W_{1/2}$, half width and f_i , fraction of ionic interaction.

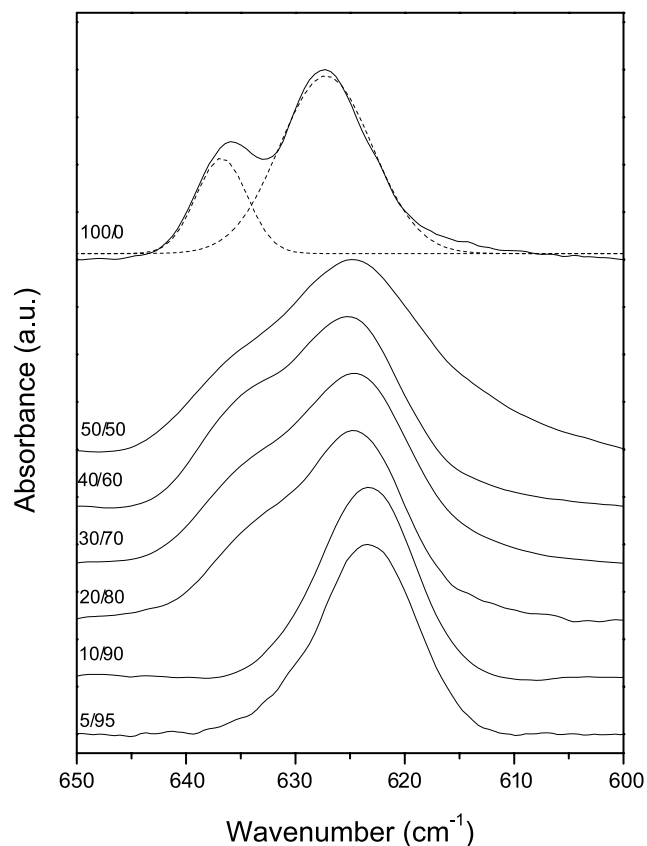


Fig. 5. FTIR spectra, presenting the region 650–600 cm^{-1} , of the weight fraction zinc salt/PVP blends.

addition, the resonance of the C1 atom is practically independent of the concentration of the zinc salt, which is consistent with our argument because this carbon atom is located far from the coordinating groups.

3.4. Proton spin lattice relaxation time in the rotating frame analyses

We examined the spin lattice relaxation times in the rotating frame ($T_{1\rho}^H$) to measure the homogeneity of the zinc salt/PVP blends on the molecular scale. According to the spin locking mode employed in this study, the magnetization of resonance is expected to decay according to the exponential function model

$$M_\tau = M_0 \exp[-\tau/T_{1\rho}^H] \quad (2)$$

where $T_{1\rho}^H$ is the spin lattice relaxation time in the rotating frame, τ is the delay time used in the experiment, and M_τ is the corresponding resonance. The value of $T_{1\rho}^H$ can be obtained from the slope of the plot of $\ln(M_\tau/M_0)$ versus τ . Figure 7 shows the $T_{1\rho}^H$ relaxation behaviors of these blends (PVP, 176 ppm) and reveals that both pure PVP and the zinc salt/PVP blends exhibit only a single relaxation throughout the whole range of blends, which indicates the good miscibility and dynamic homogeneity of the PVP phase. Table 5 summarizes the values of $T_{1\rho}^H$ derived from the

Table 3
Curve fitting of the area fractions of the free and ion-paired perchlorate ions as determined from the FTIR spectra of zinc salt/PVP blends recorded at 120 °C

wt%, Zn salt/PVP	Free ClO ₄ ⁻			Ion pair ClO ₄ ⁻		
	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_f (%)	ν (cm ⁻¹)	$W_{1/2}$ (cm ⁻¹)	A_i (%)
5/95	624	9	100	–	–	–
10/90	624	9	100	–	–	–
20/80	625	10	84.1	635	8	15.9
30/70	625	12	83.8	636	7	16.2
40/60	626	12	79.4	636	6	20.6
100/0	627	9	77.7	637	5	22.3

ν , wavenumber; $W_{1/2}$, half width.

Table 4
Chemical shifts (ppm) observed in the ¹³C CP/MAS/DD spectra of PVP and its zinc salt blends

Zn Salt (wt%)	C-1	C-2	C-4 and C-5	C-6
0	19.02	32.17	43.90	176.58
5	19.02	32.37	44.10	176.98
10	19.02	32.38	44.11	177.20
20	19.02	32.57	44.30	177.59
30	19.02	32.77	44.31	177.99
40	19.02	32.98	44.32	178.60

binary exponential analysis. The blend exhibits a single exponential and the value of $T_{1\rho}^H$ decreases upon increasing the zinc content. This observation indicates that the domain size of the zinc salt/PVP blends decreases, based on one

dimension spin-diffusion equation [21], as a result of the strong ion–dipole interactions between the zinc cations and the carbonyl groups. In addition, $T_{1\rho}^H$ is a measure of the chain mobility, the deeper slopes suggest that the chain become stiffer (less mobile) due to the increase in physical cross-link density caused by ionic complexation.

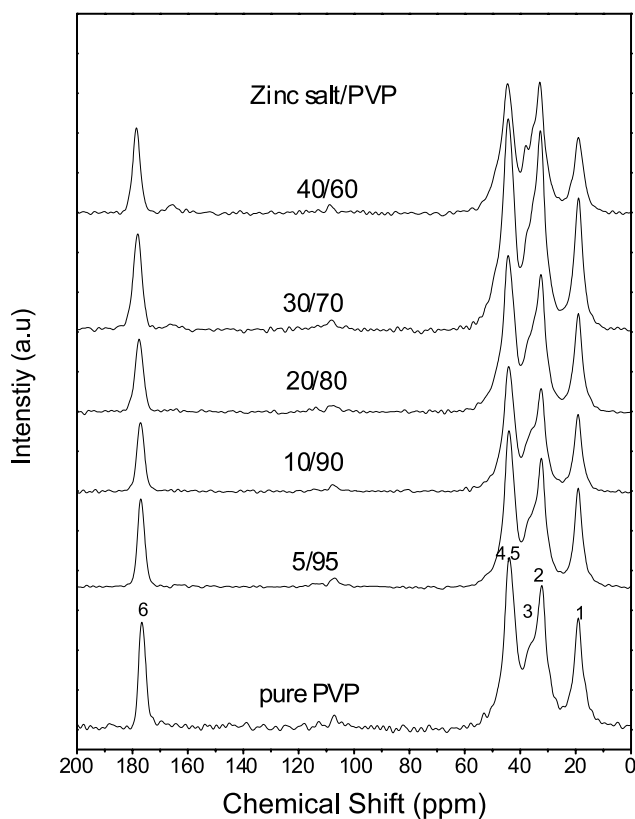
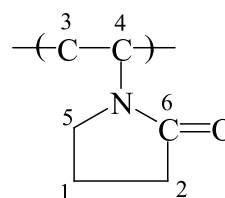


Fig. 6. ¹³C CPMAS spectra of weight fraction of the zinc salt/PVP blends recorded at room temperature.

3.5. Comparisons with hydrogen bonding systems

Fig. 8 shows the carbonyl stretching region, ranging from 1550 to 1730 cm⁻¹, of the FTIR spectra of various pyrrolidone-containing systems recorded at room temperature: 0.1 M ethylpyrrolidone (EPr, a model compound for PVP) in cyclohexane [6], PAS74-co-PVP26 copolymer [6], pure PVP, PVPh74/PVP26 blend [5], PVPh74-co-PVP26 copolymer [6], and the zinc salt/PVP (40:60) blend. The wavenumber and half-width significantly depend upon dipole interactions and hydrogen bonding and ionic interactions in and between the polymer chains. The carbonyl stretching band of the EPr solution is positioned at a higher wavenumber than that of the pure PVP because of decreased probability of carbonyl–carbonyl interactions. Similarly, the half-width of the band for pure PVP at 1680 cm⁻¹ is decreased and shifted to higher wavenumber



Scheme 1. Chemical structure of PVP and its atom numbering scheme.

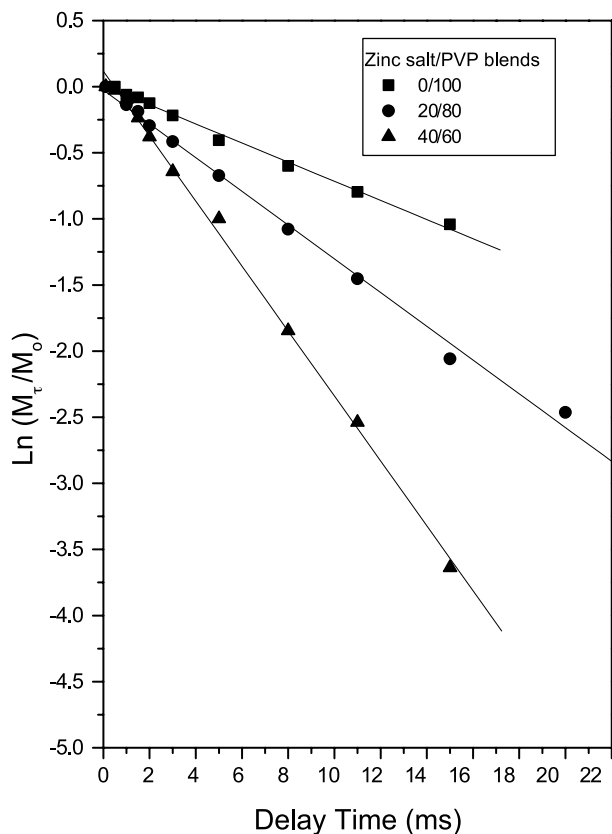


Fig. 7. Semi-logarithmic plots of the magnetization intensities of the signal at 176 ppm versus the delay time for the zinc salt/PVP blends at a contact time of 1 ms.

(1682 cm^{-1}) when the acetoxystyrene monomer is incorporated into the PVP chain (PAS74-*co*-PVP26). After deacetylation of PAS-*co*-PVP into PVPh-*co*-PVP, however, the carbonyl group absorption shifts from 1682 to 1651 cm^{-1} ; this shift is attributed to the formation of hydrogen bonds between the vinylphenol and vinylpyrrolidone segments of the copolymer. In contrast, the same carbonyl stretching frequency of the PVPh/PVP blend shifts to only 1660 cm^{-1} . This observed difference can be interpreted as suggesting that the number and/or strength of the hydrogen bonds within the PVPh-*co*-PVP copolymer are greater than those in the corresponding PVPh/PVP blend. In addition, the carbonyl band of the zinc salt/PVP = 40/60 blend has the relatively lowest wavenumber at 1615 cm^{-1} . Similar results are also observed in the solid-state NMR spectroscopic analysis shown in Fig. 9 [5,6]: the carbonyl carbon atoms' resonance in the zinc salt/PVP

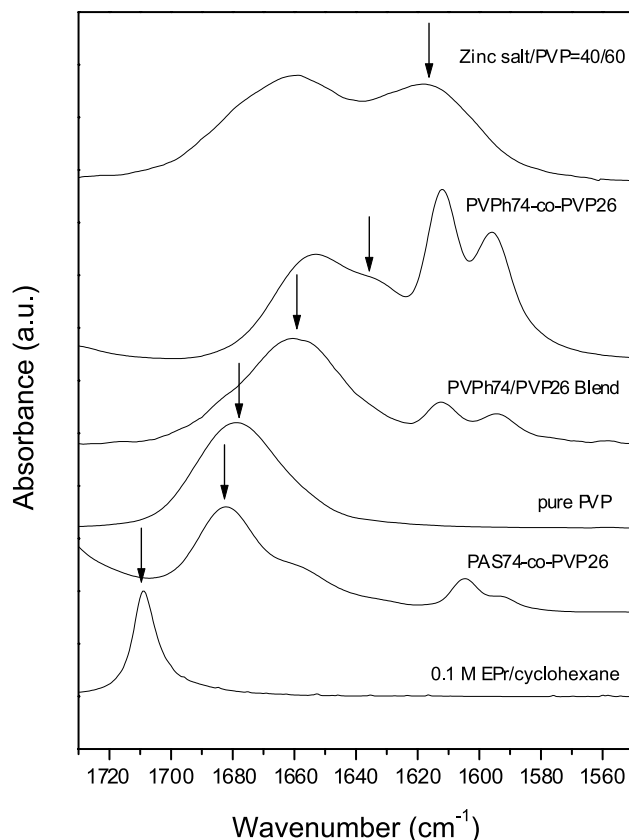


Fig. 8. FTIR spectra, recorded at room temperature and displaying the region 1730–1550 cm^{-1} , of 0.1 M ethylpyrrolidone (EPr, a model compound for PVP) in cyclohexane, PAS74-*co*-PVP26 (mol%) copolymer, pure PVP, PVPh74/PVP26 (mol%) blend, PVPh74-*co*-PVP26 (mol%) copolymer, and the zinc salt/PVP (40:60) blend.

blends experiences the greatest downfield shift, when compared with the other hydrogen bonding systems. Clearly, the FTIR and solid-state NMR spectroscopic analyses indicate the relative strength of the specific interactions: zinc salt/PVP blend > PVPh-*co*-PVP copolymer > PVPh/PVP blend > pure PVP > PAS-*co*-PVP copolymer.

4. Conclusions

The glass transition temperatures of PVP are increased by 47 °C relative to that of pure PVP when it is blended with zinc perchlorate at 40 wt%. We calculate the interaction strength of the zinc salt/PVP blend to be 1.50 based on an extended configuration entropy model equation. The IR and

Table 5

Values of $T_{1\rho}^H$ of pure PVP and its various zinc salt blends determined from proton spin lattice relaxation experiments performed at room temperature

Zn/PVP	C-1	C-2	C-4 and C-5	C-6
0/100	13.98	15.21	14.37	11.96
20/80	7.71	7.13	7.59	6.79
40/60	4.28	4.00	4.19	4.35

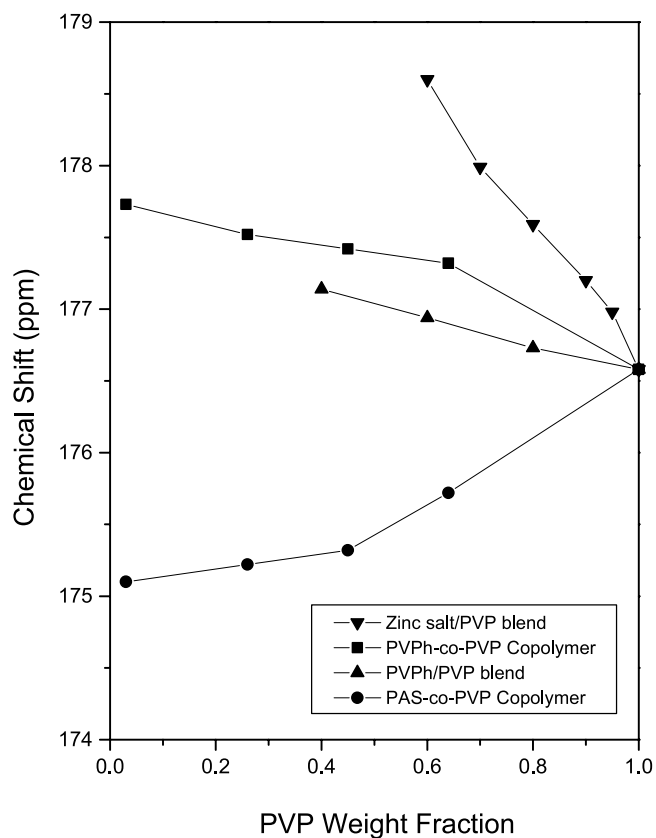


Fig. 9. Dependence of the chemical shift of the carbonyl carbon atoms on the compositions of the PAS-co-PVP copolymer, the PVPh/PVP blend, the PVPh-co-PVP copolymer, and the zinc salt/PVP blend.

solid-state NMR spectroscopic data shows that the PVP has the ability to interact ionically with the zinc salt; these interactions are stronger than those present in related hydrogen bonding systems.

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