

# Specific interactions in miscible polymer blends of poly(2-hydroxypropyl methacrylate) with polyvinylpyrrolidone

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**Abstract:** The miscibility behaviour and hydrogen-bonding interaction in blends of poly(2-hydroxypropyl methacrylate) (PHPMA) with polyvinylpyrrolidone (PVP) were characterized using differential scanning calorimetry and Fourier-transform infrared spectra. This polymer blend was miscible over the whole composition range and an unusually large positive deviation of  $T_g$  from the linearity rule was observed, indicating strong hydrogen bonding between the hydroxyl group of PHPMA and the carbonyl group of PVP. Infrared spectroscopic analysis provided positive evidence for the intra-molecular hydrogen bonding of PHPMA and inter-molecular hydrogen bonding between PHPMA and PVP at various compositions and temperatures. Furthermore, equilibrium constants and enthalpies of self-association and inter-association between functional groups in the blend of PHPMA and PVP were calculated to explain the results.

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**Keywords:** miscibility behaviour; hydrogen bonding; PHPMA; PVP

## INTRODUCTION

Miscible polymer blends have been of great interest to material scientists as a result of improved or modified physical properties of the individual constituent polymers. However, from a thermodynamic viewpoint, miscibility behaviour is rarely achieved in polymer blends owing to the high degree of polymerization that provides a small entropy change. As a result, the formation of miscible polymer blends can be achieved through specific interactions, such as hydrogen bonding,<sup>1–3</sup> ionic interaction,<sup>4–6</sup> charge-transfer complex formation, and a copolymer repulsion effect.<sup>7–9</sup> In general, hydrogen-bonding interaction is considered to be the driving force for miscibility and its important role in the miscibility of polymer blends has been widely described. In earlier studies,<sup>1–3</sup> hydrogen-bonded donor polymers can be divided into two categories. The first category is the simple self-association polymers, such as nylons and polyurethanes, which have both donor and acceptor functional groups. The two-equilibrium-constant model for self-association polymers gives rise to the second category of polymers, such as polyvinylphenol (PVPh), phenolic resin, phenoxy resin and poly(vinyl alcohol), because the self-association equilibrium constant describing dimer formation should be different from that for multimer formation, based on infrared spectra analysis.<sup>1</sup>

Poly(2-hydroxypropyl methacrylate) (PHPMA) has a special chemical structure that includes the hydroxyl donor group and the carbonyl acceptor group. We consider that this polymer is a simple self-association polymer, like the nylons or polyurethanes. As far as we know, few studies have been reported concerning the hydrogen bond that exists between the PHPMA and second functional polymers. Goh and coworkers<sup>10</sup> studied the PHPMA complexation with three tertiary amide polymers containing poly(*N*-methyl-*N*-vinylacetamide), poly(*N,N*-dimethylacrylamide) and poly(2-ethyl-2-oxazoline). Katime and coworkers<sup>11</sup> also studied the hydrogen bonding between PHPMA and polyvinylpyridines. However, the self-association equilibrium constant of PHPMA and the inter-association equilibrium with the functional group of the second polymer have not been investigated. In this present study, we determine the self-association equilibrium constant of PHPMA and the inter-association equilibrium constant between the PHPMA and the polyvinylpyrrolidone (PVP).

Polyvinylpyrrolidone is a water-soluble tertiary amide and a strong Lewis base that possesses good biocompatibility, and devices based on hydrogels of this material have found several medical applications. PVP was chosen for this study because the amide group is known to be a stronger hydrogen-bond acceptor

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Contract/grant sponsor: National Science Council, Taiwan, Republic of China; contract/grant number: NSC-91-2216-E-009-018  
(Received 31 October 2002; accepted 20 March 2003)

than the carbonyl group of poly(methyl methacrylate) (PMMA) or the ether group of poly(ethylene oxide) (PEO). It has been shown to form miscible blends with a large number of polymers such as polyvinylphenol,<sup>12</sup> phenoxy resins,<sup>13</sup> poly(vinyl alcohol),<sup>14</sup> poly(vinyl fluoride)<sup>15</sup> and poly(vinyl chloride).<sup>16</sup> In our previous study, we have found that the wavenumber and half-width of PVP absorptions in the infrared spectral analysis are sensitive to the dipole interaction or hydrogen bonding with molecules or polymer chains. Furthermore, the glass transition temperatures of PVP-based polymer blends or copolymers have a good correlation with these specific interactions.<sup>17</sup>

In this study, the polymer blend of PHPMA with PVP was investigated using differential scanning calorimetry (DSC) and Fourier-transform infrared spectrum (FTIR). In addition, equilibrium constants and enthalpies of self-association and inter-association between functional groups in blends of PHPMA and PVP were calculated to explain the experimental results of these blends.

## EXPERIMENTAL

### Materials

The poly(2-hydroxypropyl methacrylate) (PHPMA) was purchased from Aldrich Chemical Company with molecular weights of  $M_n = 24\,000$  and  $M_w = 32\,700\text{ g mol}^{-1}$ . The polyvinylpyrrolidone (PVP) with molecular weight of  $M_w = 58\,000\text{ g mol}^{-1}$  was purchased from Acros Chemical Company, Inc.

### Preparation of polymer blends

Solution blends (5% wt/vol) of PHPMA and PVP in *N,N*-dimethylformamide were prepared by mixing appropriate amounts of each polymer. Each solution was allowed to evaporate slowly at 50 °C for 1 day. The film of each blend was then dried at 80 °C for 2 days to ensure total elimination of solvent.

### Thermal analysis

Differential scanning calorimetry was performed with a Du-Pont (DSC-9000) instrument. Sample weights of 5–10 mg, and a heating rate of 20 °C min<sup>-1</sup> were used. The sample was first heated from 30 °C to 210 °C and kept at that temperature for 10 min. It was then quickly cooled to 30 °C in the DSC cell and maintained at that temperature for another 3 min. The glass transition temperature was then obtained as the inflection point of the increase in heat capacity with a scan rate of 20 °C min<sup>-1</sup> temperature range of 30 to 250 °C.

### FTIR spectroscopy

Infrared spectra were measured on a Nicolet Avatar 320 FTIR spectrophotometer and 32 scans were collected with a spectral resolution 1 cm<sup>-1</sup>. Infrared spectra of polymer blend films were determined by using the conventional NaCl disk method. The DMF solution containing the blend was cast onto

a NaCl disk and dried under conditions similar to those used in the bulk preparation. Films used in the FTIR measurements were sufficiently thin to be within the absorbance range where the Beer–Lambert law was obeyed. IR spectra recorded at elevated temperatures were obtained by using a cell mounted inside the temperature-controlled compartment of the spectrometer.

## RESULTS AND DISCUSSION

### Thermal analysis

The most widely used criterion for the judgment of the miscibility behaviour of polymer blend is the existence of a single glass transition temperature. The  $T_g$  dependence on composition is shown in Fig 1. All PHPMA/PVP blends have only a single  $T_g$ , suggesting that these are fully miscible blends with a homogeneous amorphous phase. Moreover, a single  $T_g$  higher than that of either individual polymer was observed. This large positive deviation reveals that strong hydrogen bonding must exist between these two polymers. It has been generally suggested that the  $T_g$  relationship to the composition of the miscible polymer blends follows the Kwei equation:<sup>18</sup>

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 \quad (1)$$

where  $w_1$  and  $w_2$  are weight fractions of the components,  $T_{g1}$  and  $T_{g2}$  represent the corresponding glass transition temperatures, and  $k$  and  $q$  are fitting constants. In this study,  $k = 1$  and  $q = 130$  were

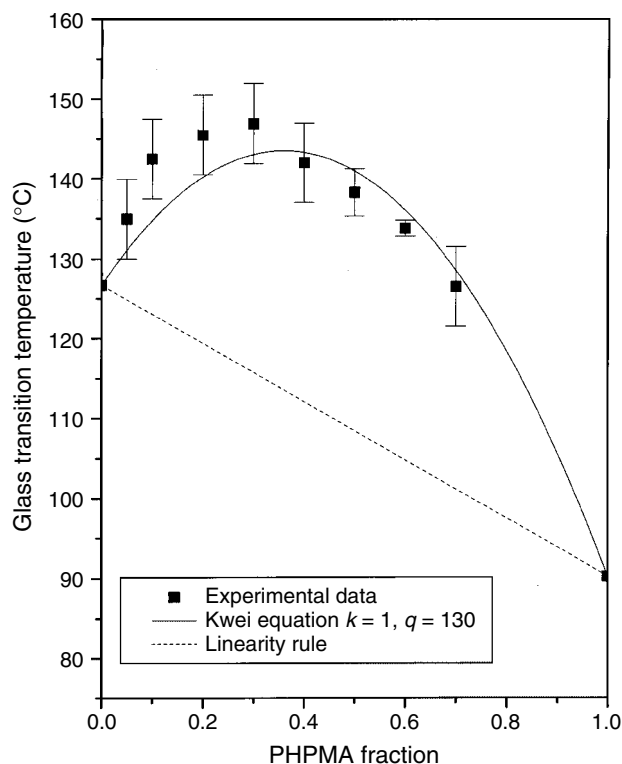


Figure 1.  $T_g$  versus composition curves based on: (■) experimental data and (—) Kwei equation.

obtained from the non-linear least-squares ‘best fit’ values. Here  $q$  is a parameter corresponding to the strength of hydrogen-bonding in the blend, reflecting a balance between the breaking of the self-association and the forming of the inter-association hydrogen bonding. In this study, a positive  $q$  value of 130 was obtained, indicating a strong intermolecular interaction between PHPMA and PVP. In our previous study,<sup>12</sup> we found that the  $q$  value of PVPh/PVP blend was 140; we therefore expect that the hydrogen bonding strength of the PHPMA/PVP blend is slightly weaker than that of the PVPh/PVP blend.

### Infrared spectroscopy analysis

The chemical structure of the pure PHPMA has both a donor hydroxyl group and an acceptor carbonyl group. If we can make a suitable infrared measurement using the pure PHPMA, the self-association equilibrium constant of pure PHPMA can be determined by using the following simple equation:<sup>1</sup>

$$K_B = \frac{f_{HB}}{(f_F)^2} \quad (2)$$

where the  $K_B$  is the self-association equilibrium constant of pure PHPMA, and  $f_{HB}$  and  $f_F$  represent the fractions of hydrogen-bonded and free carbonyl groups of the PHPMA, respectively. Figure 2 illustrates the FTIR spectra of the pure PHPMA measured at temperatures from 130 °C to 180 °C. We chose these high temperatures because they are above the glass transition temperature of the PHPMA, so that equilibrium conditions can be retained. Figure 2(a) shows the hydroxyl-stretching region of the pure PHPMA at various temperatures. The pure PHPMA shows a narrow half-width hydroxyl stretching, revealing that the hydrogen-bonded conformation is simpler between the hydroxyl and the carbonyl of the PHPMA.

In contrast, the pure phenolic resin or polyvinylphenol shows a very broad hydroxyl stretching region (the two-equilibrium-constant model for self-association polymers). The half-width of hydroxyl-stretching of the pure PHPMA is similar to that of nylon 6 or polyurethanes (simple self-association polymers) showing a very narrow absorption.<sup>1</sup> In addition, the hydrogen-bonded hydroxyl band of the pure PHPMA tends to shift to a higher frequency, from 3512 cm<sup>-1</sup> to 3532 cm<sup>-1</sup>, with increasing temperature, indicating that the hydrogen bonding is decreased with increasing temperature, and this has been well documented.

Figure 2(b) shows that the carbonyl-stretching frequency of the pure PHPMA splits into two bands,<sup>9</sup> absorptions by the free and hydrogen-bonded carbonyl groups at 1730 and 1710 cm<sup>-1</sup>, respectively. These two bands can easily be resolved into two Gaussian peaks, as shown in Fig 2(c), and the ratio of these two absorptivities ( $a = a_2/a_1$ ) is equal to 1.5, according to previous infrared studies of hydroxyl-carbonyl inter-association.<sup>1</sup> The curve-fitting results are summarized in Table 1, indicating that the hydrogen-bonded fraction of the carbonyl groups decreased with the increase of temperature. Therefore, the self-association equilibrium constant of pure PHPMA can be determined using eq (2), and its corresponding hydrogen-bonding enthalpy can be determined by the Van't Hoff relationship

$$K = -\frac{\Delta h}{RT} + C \quad (3)$$

Meanwhile, the self-association equilibrium constant in this temperature range based on the Van't Hoff expression can be calculated and extrapolated to room temperature as shown in Fig 3. We obtained the self-association equilibrium constant at 25 °C ( $K_B$ ) of the pure PHPMA as 3.17 and its hydrogen-bonding enthalpy ( $\Delta h$ ) as -3.16 Kcal mol<sup>-1</sup>. The

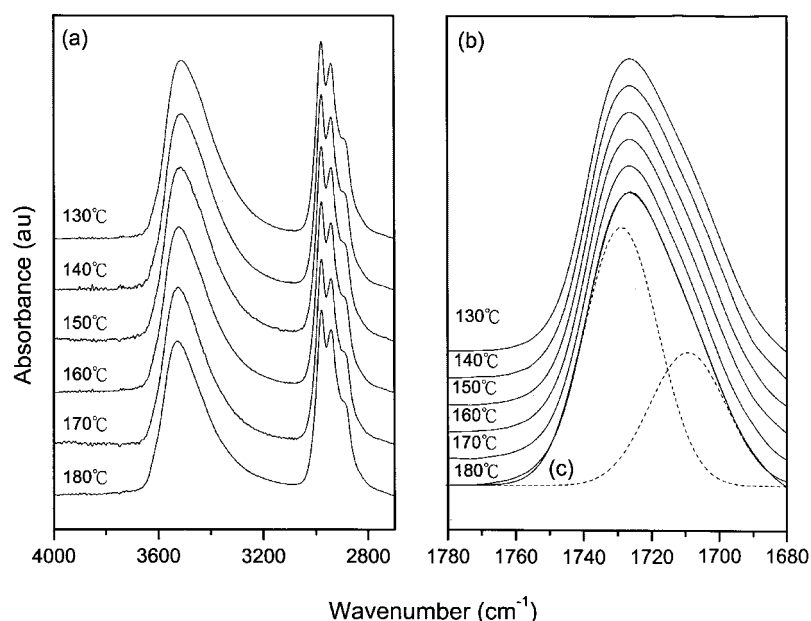


Figure 2. FTIR spectra recorded at various temperatures for pure PHPMA.

**Table 1.** Curve-fitting of fraction of hydrogen-bonding results of the pure PHPMA at various temperatures

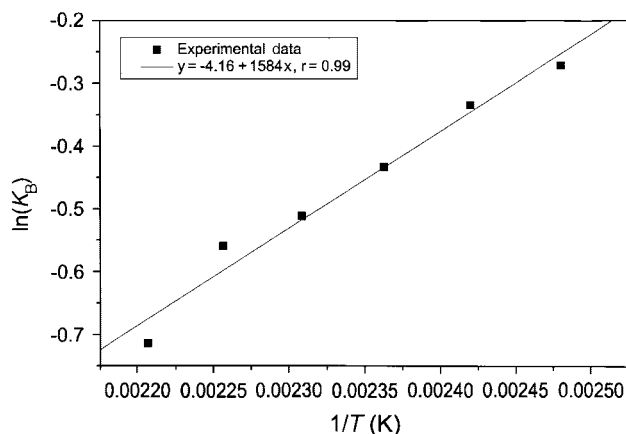
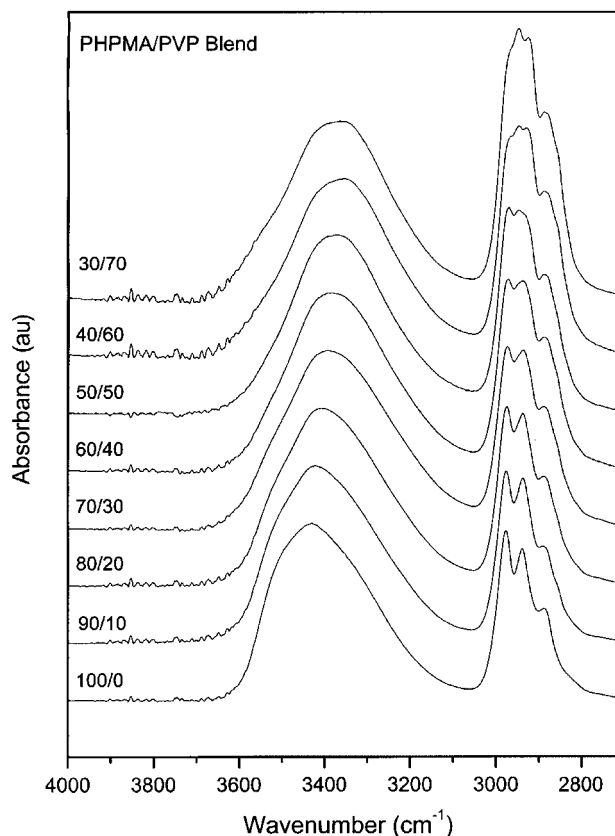
Pure PHPMA	Free C=O			H-bonded C=O			
	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$A_f$ (%)	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$A_b$ (%)	$f_b$ (%) <sup>*</sup>
130	1729.6	20.0	56.85	1710.0	23.2	43.15	33.60
140	1729.5	20.2	58.00	1710.0	23.3	42.00	32.56
150	1729.3	20.5	59.82	1709.7	22.8	40.18	30.94
160	1729.3	20.8	61.26	1709.9	23.0	38.74	29.67
170	1729.2	21.1	62.13	1709.8	22.9	37.87	28.90
180	1728.9	21.6	64.93	1709.3	22.6	35.07	26.50

\*  $f_b$ : fraction of hydrogen bonding.

relatively smaller self-association equilibrium constant observed for the pure PHPMA compared with the pure polyvinylphenol ( $K_B = 66.8$ )<sup>1</sup> reveals a greater steric-hindrance effect in the pure PHPMA.

We now turn our attention to the hydrogen-bonded blends of PHPMA/PVP; Fig 4 shows a scale-expanded infrared spectrum in the range 2700–4000 cm<sup>-1</sup> of a PHPMA/PVP blend at room temperature. The pure PHPMA shows two bands in the hydroxyl-stretching region of the infrared spectrum, corresponding to free hydroxyl at 3525 cm<sup>-1</sup> and the hydrogen-bonded hydroxyl–carbonyl of the PHPMA at 3430 cm<sup>-1</sup>, respectively. The frequency difference between the hydrogen-bonded hydroxyl absorption and free hydroxyl absorption ( $\Delta\nu$ ) is a rough estimate of the average hydrogen-bonding strength and its enthalpy in a hydrogen-bonding blend system.<sup>19</sup> Compared with the polyvinylphenol/poly(methyl methacrylate) blend system, the  $\Delta\nu$  is about 125 cm<sup>-1</sup>,<sup>1</sup> corresponding to a hydrogen-bonding enthalpy of  $-3.75$  Kcal mol<sup>-1</sup>. In this study, the  $\Delta\nu$  of the pure PHPMA is 95 cm<sup>-1</sup>, corresponding to a hydrogen-bonding enthalpy of about  $-3.16$  Kcal mol<sup>-1</sup>, which is in good agreement with previous infrared spectra analysis, with measurement at various temperatures.

Figure 4 also illustrates that the hydrogen-bonded hydroxyl and carbonyl group absorbance of PHPMA shifts to a lower wavenumber with increase of the PVP content. Concurrently, the intensity of the free hydroxyl group decreases gradually with an increase of PVP content, as would be expected. This

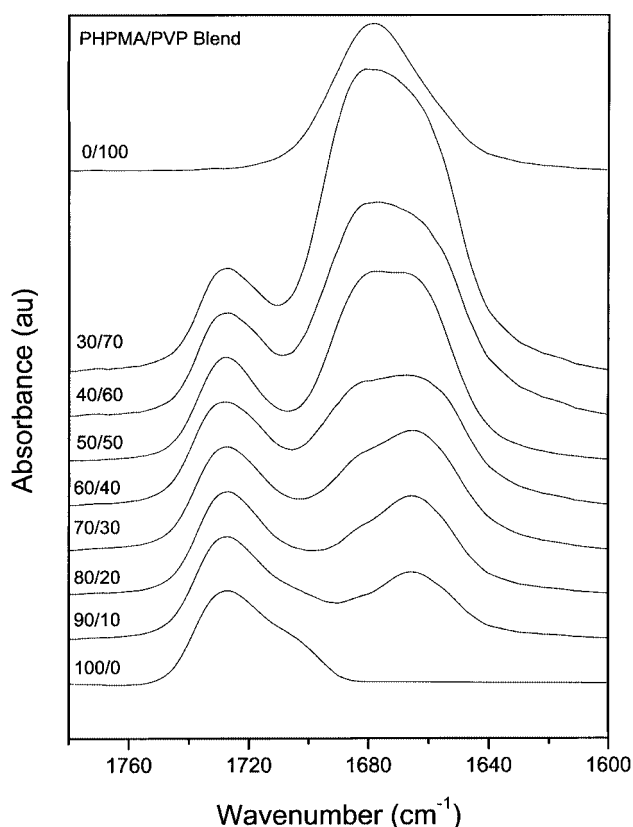
**Figure 3.** The Van't Hoff relationship for pure PHPMA.**Figure 4.** FTIR spectra recorded at room temperature in the 4000–2700 cm<sup>-1</sup> region for PHPMA/PVP blends.

result reflects a new distribution of hydrogen bond formation resulting from the competition between the hydroxyl–carbonyl group of pure PHPMA and the hydroxyl of PHPMA and the carbonyl of PVP. It also reveals that the interaction of the hydroxyl of PHPMA and the carbonyl of PVP become dominant in PVP-rich blends. Therefore, it is reasonable to assign the band at 3350 cm<sup>-1</sup> to the hydrogen-bonding interaction between the hydroxyl of PHPMA and carbonyl group of PVP. Hydrogen-bonding interaction between hydroxyl of PHPMA and carbonyl of PVP ( $\Delta\nu = 175$  cm<sup>-1</sup>) is stronger than the hydroxyl–carbonyl interaction of the pure PHPMA ( $\Delta\nu = 95$  cm<sup>-1</sup>) and this is consistent with the observed positive  $q$  value in the Kwei equation. In the PVPh/PVP blend, the  $\Delta\nu$  is 325 cm<sup>-1</sup>, which provides even stronger hydrogen-bonding interaction

than that of the PHPMA/PVP blend, which is also consistent with the  $q$  value difference in the Kwei equation. The  $\Delta\nu$  of PHPMA/PVP blend is  $175\text{ cm}^{-1}$ , which is equal to the  $\Delta\nu$  of the pure PVP.<sup>12</sup> Therefore, the inter-association hydrogen-bonding enthalpy of PHPMA/PVP is about  $-5.2\text{ Kcal mol}^{-1}$  from this relationship.

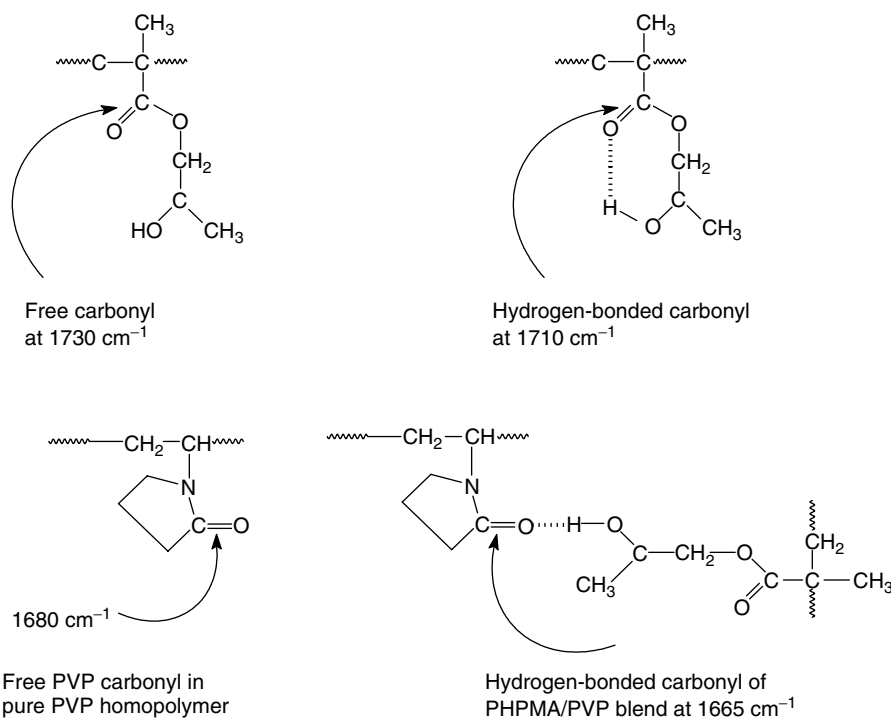
Figure 5 shows infrared spectra of the carbonyl stretching recorded at room temperature, ranging from  $1600$  to  $1780\text{ cm}^{-1}$  for the blends with various compositions. There are numerous possible interactions involved and the four most important are summarized in Scheme 1. As mentioned above, the carbonyl stretching of pure PHPMA splits into two bands, absorption by the free and hydrogen-bonded carbonyl groups at  $1730$  and  $1710\text{ cm}^{-1}$ , respectively. Meanwhile, the carbonyl stretching of PVP also splits into two bands at  $1680$  and  $1665\text{ cm}^{-1}$ , corresponding to the free and the hydrogen-bonded carbonyl groups, which can also be well fitted to a Gaussian function. The fraction of hydrogen-bonded carbonyl group of PVP can be calculated by using an appropriate absorptivity ratio ( $a_R = a_{\text{HB}}/a_{\text{F}} = 1.3$ ) which has been discussed in our previous study.<sup>12</sup>

Table 2 summarizes results from these curve fittings, indicating that the carbonyl hydrogen-bonded fraction of PVP increases with the increase of the PHPMA content. Furthermore, the carbonyl of PVP shifts to only about  $1665\text{ cm}^{-1}$ , which is a smaller frequency than that of the PVP/PHPMA blend ( $1660\text{ cm}^{-1}$ ). This result is also consistent with the Kwei equation and analysis of infrared spectra on hydroxyl-stretching. Here, we need to emphasize that the fraction of hydrogen-bonded carbonyl of PHPMA cannot be calculated due to the overlapping with the



**Figure 5.** FTIR spectra recorded at room temperature in the  $1780$ – $1600\text{ cm}^{-1}$  region for PHPMA/PVP blends.

free carbonyl of the PVP. However, we expect that the hydrogen-bonded carbonyl fraction will decrease with the increase of PVP content because most hydroxyl groups of the PHPMA will interact with the carbonyl

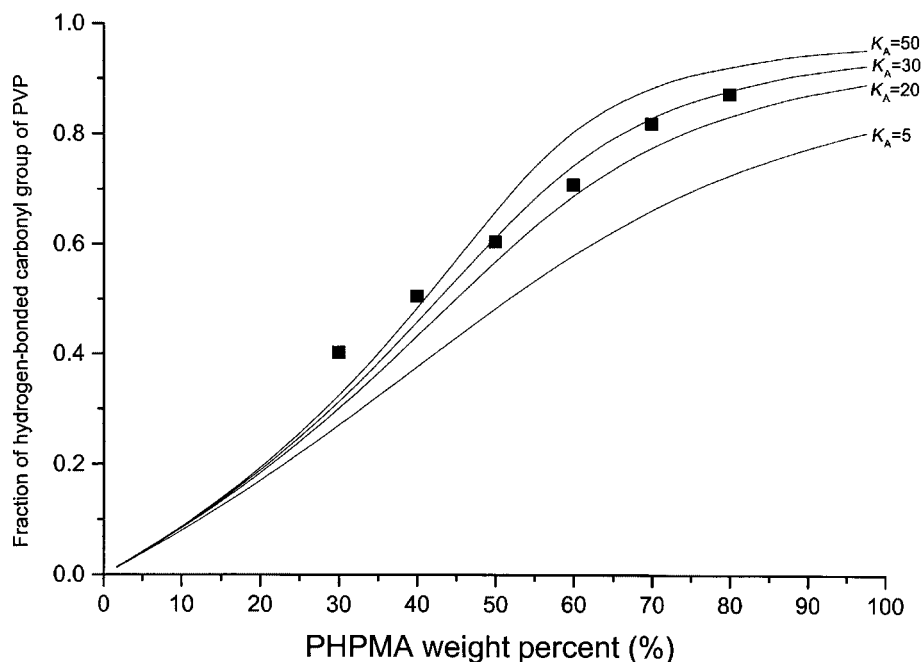


**Scheme 1.**

**Table 2.** Curve fitting of fraction of hydrogen-bonding results of the PHPMA/PVP blends at room temperature

PHPMA/PVP	Free C=O			H-bonded C=O			$f_b$ (%) <sup>*</sup>
	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$A_f$ (%)	$\nu$ (cm <sup>-1</sup> )	$W_{1/2}$ (cm <sup>-1</sup> )	$A_b$ (%)	
80/20	1682.7	16.3	10.07	1663.5	22.0	89.93	87.30
70/30	1684.5	12.5	14.53	1663.6	27.1	85.47	81.91
60/40	1683.7	16.3	24.07	1661.7	25.0	75.93	70.82
50/50	1684.4	14.5	33.46	1665.0	24.7	66.54	60.48
40/60	1684.1	15.5	32.97	1663.9	27.1	57.03	50.52
30/70	1683.7	16.8	53.31	1663.4	21.5	46.69	40.26

<sup>\*</sup>  $f_b$ : fraction of hydrogen bonding.

**Figure 6.** Experimental values of hydrogen-bonded carbonyl group of PVP and the theoretical curves obtained by using different values of  $K_A$ .

of PVP. From Table 2, we can calculate the inter-association equilibrium constant of the PHPMA/PVP blend. This investigation attempted to use the approximate method proposed by Coleman *et al* to obtain the  $K_A$  value, expressed by eqns (4) and (5):<sup>1</sup>

$$\Phi_B = \frac{\Phi_{B1}}{(1 - K_B \Phi_{B1})^2} \left[ 1 + \frac{K_A \Phi_{0A}}{r} \right] \quad (4)$$

$$\Phi_A = \Phi_{0A} \left[ 1 + \frac{K_A \Phi_{B1}}{(1 - K_B \Phi_{B1})} \right] \quad (5)$$

where  $\Phi_A$  and  $\Phi_B$  are volume fractions of the non-self-associated species A and the self-associating species B, respectively.  $\Phi_{0A}$  and  $\Phi_{B1}$  are the corresponding volume fractions of isolated PVP and PHPMA segments, respectively, and  $r$  is the ratio of molar volumes,  $V_A/V_B$ . The self-association equilibrium constants ( $K_B$ ), describe the formation of hydrogen bonding.

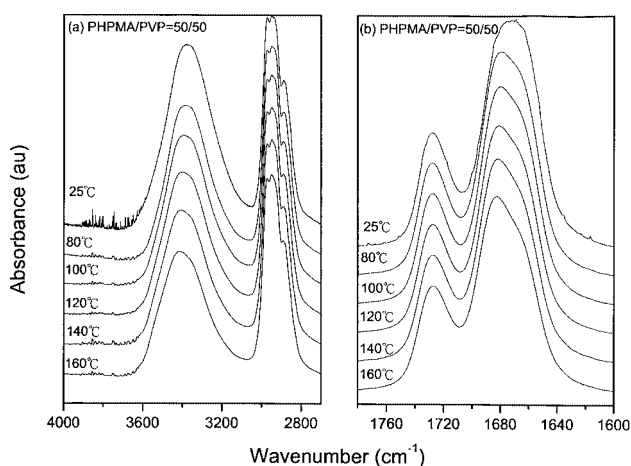
Finally, the  $K_A$  is the equilibrium constant describing the association of A with B. In the first place, we calculated the theoretical fraction of hydrogen-bonded carbonyls in the blend from eqns (4) and (5) by using different values of  $K_A$ . We then plotted such values

as a function of the blend composition and compared them with the experimental data from Table 2. Figure 6 shows that a reasonable value of  $K_A$  of 30 is obtained from the data-fitting of the theoretical prediction by using Miscibility Guide & Phase Calculator (MG&PC) Software package.<sup>1</sup> Table 3 lists these equilibrium constants and their enthalpies, molar volumes, molecular weights, and solubility parameters of PHPMA and PVP required by the Painter–Coleman equation to estimate thermodynamic properties for the polymer blend. The path from the hydrogen-bonding equilibrium concentrations through to the fraction of hydrogen bonded carbonyl has been widely described by Coleman *et al*.<sup>1</sup> These results reveal that the inter-association hydrogen bonding between the hydroxyl group of PHPMA and carbonyl group of the PVP is stronger than the self-association hydrogen bonding between the hydroxyl and carbonyl group of the pure PHPMA, which is consistent with previous Kwei equation and infrared spectrum analysis.

Figure 7(b) shows the FTIR spectra of the PHPMA/PVP = 50/50 blend measured at temperatures from 25 °C to 180 °C, revealing that the fraction

**Table 3.** Summary of the self-association and inter-association parameters of PHPMA/PVP blend

			Equilibrium constant $K$ (25 °C)	Enthalpy, $\Delta h$ (Kcal mol <sup>-1</sup> )
Self-association of PHPMA <sup>1</sup>			3.17	-3.16
Inter-association between PHPMA and PVP <sup>1</sup>			30.0	-5.20
Polymer	Molar volume (ml mol <sup>-1</sup> )	Molecular weight (g mol <sup>-1</sup> )	Solubility parameter (cal ml <sup>-1</sup> ) <sup>0.5</sup>	Degree of polymerization DP
PHPMA <sup>2</sup>	108.4	143.2	9.4	170
PVP <sup>2</sup>	73.6	115.1	11.0	500

<sup>1</sup> In this study.<sup>2</sup> Estimated using a group contribution method proposed by Coleman *et al.*<sup>1</sup>**Figure 7.** FTIR spectra recorded at various temperatures for PHPMA/PVP = 50/50 blend.

of hydrogen-bonded carbonyl group decreases with the increase of temperature at the same composition. Figure 7(a) also shows the hydroxyl-stretching region of PHPMA/PVP = 50/50 at various temperatures. The hydrogen-bonded hydroxyl-carbonyl of the PHPMA shifts to a higher frequency obviously with increase of temperature, suggesting that the inter-association hydrogen bonding between PHPMA and PVP becomes weaker with the temperature increase. Furthermore, the change in total area is thus explained on the basis of the difference in the average absorption coefficients for the free and hydrogen-bonded hydroxyl-stretching vibration.

## CONCLUSIONS

PHPMA/PVP blends are totally miscible over the entire composition range based on DSC analysis and the Kwei equation can accurately predict  $T_g$  values from experimental results due to the existence of hydrogen bonding between the hydroxyl group of PHPMA and the carbonyl group of PVP. Infrared spectra provides positive evidence of the hydrogen bonding at various compositions and with various inter- and intra-molecular interactions. The inter-association constant for the PHPMA/PVP blend is

significantly higher than the self-association constant of pure PHPMA, revealing that the tendency toward hydrogen bonding of the PHPMA and PVP dominates the intra-hydrogen bonding of the pure PHPMA in the mixture based on FTIR and DSC analysis.

## ACKNOWLEDGMENTS

The authors would also like to thank the National Science Council, Taiwan, Republic of China for financially supporting this research under Contract No NSC-91-2216-E-009-018.

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