

## Interpolymer Complexation between Poly(*p*-vinylphenol) and Pyridine-Containing Polymers

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**ABSTRACT:** Interpolymer complexation behavior between poly(*p*-vinylphenol) (PVPh) and three pyridine-containing polymers, poly(2-vinylpyridine) (P2VPy), poly(4-vinylpyridine) (P4VPy), and poly(2-vinylpyridine-*co*-styrene) (P2VPyS) with 70% vinylpyridine repeating units was studied. PVPh forms interpolymer complexes with the three pyridine-containing polymers over the whole feed composition range in ethanol solutions. The glass transition temperatures of the interpolymer complexes are remarkably higher than those calculated from the additivity rule, indicating strong favorable intermolecular interactions between unlike polymer chains. P2VPy has a stronger complexation ability with PVPh as compared with P2VPyS, showing the important role of pyridine group in achieving interpolymer complex formation. P4VPy shows a stronger complexation ability with PVPh as compared with P2VPy, demonstrating that the stereo-structure of repeating units affects interpolymer complex formation. When using *N,N*-dimethylformamide as solvent, complexation does not occur between PVPh and the three pyridine-containing polymers. Infrared studies of the complexes show the existence of hydrogen bonds between the phenolic hydroxyl groups and the nitrogens of pyridine groups, and the strength of interaction decreases in the order P4VPy > P2VPy > P2VPyS.

**KEY WORDS** Interpolymer Complexes / Poly(*p*-vinylphenol) / Poly(2-vinylpyridine) / Poly(4-vinylpyridine) / Poly(styrene-*co*-2-vinylpyridine) /

Polymers usually require the presence of favorable interpolymer interactions in achieving miscibility, as the combinatorial entropy change is too small to produce a negative free energy of mixing. In certain cases when such specific favorable interpolymer interactions are strong enough, interpolymer complexation occurs as characterized by their peculiar viscosity, electrical conductivity and other properties. In addition, if the interpolymer interactions are superior to those between either of the polymer-solvent pairs, interpolymer complexes are obtained in the form of co-precipitation from their common solvent in which both component polymers are initially soluble.

Recently, we investigated the complexation behavior between alcoholic hydroxyl-contain-

ing polymers and tertiary amide polymers.<sup>1-3</sup> Interpolymer complexes are formed through intermolecular hydrogen bonding associations between hydroxyls and amide carbonyls which are present in different polymer chains. Pyridine-containing polymers can form hydrogen bonds with proton-donating group through sharing the valence electrons of pyridine nitrogen atoms. We<sup>4</sup> have previously reported that poly(4-vinylpyridine) (P4VPy) is immiscible with polysulfone (PSf) but is miscible with carboxylated polysulfone (CPSf) having degrees of carboxylation of 0.43—1.93, and can even form complexes in *N,N*-dimethylformamide (DMF) solutions when the feed is rich in CPSf. This result clearly indicates that there is a strong intermolecular interaction between

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pyridine groups and carboxylic acid groups which results in the miscibility and complex formation between P4VPy and CPSf. Besides, P4VPy can form interpolymer complexes with other carboxyl-containing polymers such as poly(acrylic acid) (PAA)<sup>5,6</sup> and poly(methacrylic acid) (PMAA).<sup>6</sup> P4VPy also forms complexes with poly(*p*-vinylphenol) (PVPh) in methanol solutions; it forms miscible blends with PVPh when cast from pyridine solutions.<sup>7</sup> Poly(2-vinylpyridine) (P2VPy) also forms complexes with PMAA<sup>8,9</sup> in DMF solutions. Lee and co-workers<sup>10</sup> reported that P2VPy and PVPh formed complexes in tetrahydrofuran (THF) solutions. The complexes obtained by mixing P2VPy and PVPh in the 1:1 and 1:4 ratios gave similar IR spectra and had similar glass transition temperatures. They concluded that a 1:1 molar ratio complex of P2VPy and PVPh was formed. In this report, we present our studies on the miscibility and complexation behavior of three pyridine-containing polymers, *viz.* P2VPy, P4VPy, and poly(2-vinylpyridine-*co*-styrene) (P2VPyS) containing 70% of 2-vinylpyridine repeating units with PVPh in ethanol and DMF solutions. The abilities of the three pyridine-containing polymers to form complexes with PVPh are compared using Fourier-transform infrared spectroscopy.

## EXPERIMENTAL

### Materials

PVPh, P2VPy, and P4VPy with reported weight-average molecular weights of 22.0, 20.0, and 60.0 kg mol<sup>-1</sup>, respectively, were all obtained from Polysciences, Inc. P2VPyS was purchased from Scientific Polymer Products, Inc.; the number- and weight-average molecular weights are 52.9 and 103.6 kg mol<sup>-1</sup>, respectively, by GPC measurements. The glass transition temperatures of PVPh, P2VPy, P4VPy, and P2VPyS, are 142, 70, 135, and 96°C, respectively.

### Preparation of Polymer Complexes and Blends

Interpolymer complexes between PVPy and the three pyridine-containing polymers were obtained through mixing their ethanol solutions with concentrations of 0.1 g l<sup>-1</sup> of polymer. In this work, ethanol, which can easily dissolve all the four polymers used, was chosen as their common solvent. The precipitates were separated by centrifugation, washed with solvent, and then dried *in vacuo* at 90°C to constant weight. For blends prepared by solution-casting from DMF solutions, initial removal of solvent was done on a hot plate at about 90–120°C, and the blends were then dried *in vacuo* at 90°C for at least two weeks. All the complexes and blends were stored in a desiccator to prevent absorption of moisture. The nitrogen contents of interpolymer complexes were determined by elemental analysis using a Perkin-Elmer 2400 elemental analyzer.

### Glass Transition Temperature ( $T_g$ ) Measurements

The glass transition temperatures ( $T_g$ ) of the complexes and blends were measured by a Perkin-Elmer DSC-4 differential scanning calorimeter. All the samples were preheated to 180°C and held at that temperature for 10 min to ensure complete removal of any moisture and residual solvent. The scanning rate was 20°C min<sup>-1</sup> and  $T_g$  was taken as the initial onset of the change of slope in the differential scanning calorimetry (DSC) curve. All the reported  $T_g$  values are the averages of several runs.

### Fourier-Transform Infrared (FTIR) Spectroscopic Characterization

Infrared spectra were recorded on a Perkin-Elmer 1725X FTIR spectrophotometer; sixty four scans were signal-averaged at a resolution of 2 cm<sup>-1</sup>. Spectra recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell equipped with an automatic temperature controller which was mounted on the spectrophotometer.

The sample chamber was purged with  $N_2$ . Samples for FTIR analysis were prepared by casting the DMF solutions onto KBr discs and then dried *in vacuo* at  $60^\circ\text{C}$  for at least one week.

## RESULTS AND DISCUSSION

### *Interpolymer Complexation of PVPh with Pyridine-Containing Polymers*

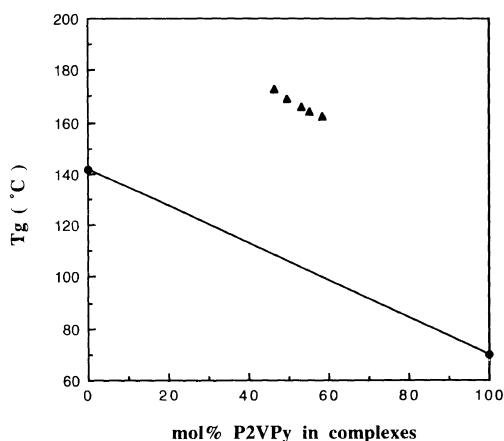
PVPh formed interpolymer complexes with the three pyridine-containing polymers in ethanol solutions. Data on the yields and compositions of the complexes between PVPh and P2VPy or P4VPy, and their  $T_g$ 's are listed in Table I.

For the PVPh/P2VPy system, interpolymer complexes occurred over the entire feed composition range in ethanol solutions. The yields of the complexes were in the range of 37–89 wt% with the maximum at the feed composition of 50 wt% of P2VPy. As shown in Table I and Figure 1, the compositions of the complexes fall in a narrow range centered at 50 mol% of P2VPy irrespective of the initial feed compositions. This result demonstrates that PVPh prefers to form 1:1 molar ratio complexes with P2VPy in ethanol solutions. The earlier work by Lee and coworkers<sup>10</sup> relied on the similarity of the IR spectra and  $T_g$  values of various complexes to reach the conclusion that PVPh and P2VPy formed 1:1 complexes in THF solutions. The  $T_g$ 's of the complexes are in the range of 162 to  $173^\circ\text{C}$  which are higher than those calculated from additivity rule by about  $60^\circ\text{C}$ , indicating strong interpolymer interactions between different polymer chains.

PVPh also formed interpolymer complexes with P4VPy throughout the entire feed composition range in ethanol solutions. The yields of the complexes were in the range from 44 to 90 wt% with the maximum at the feed composition of 50 wt% of P4VPy and were obviously higher than those of the corresponding PVPh/P2VPy complexes, indicating that

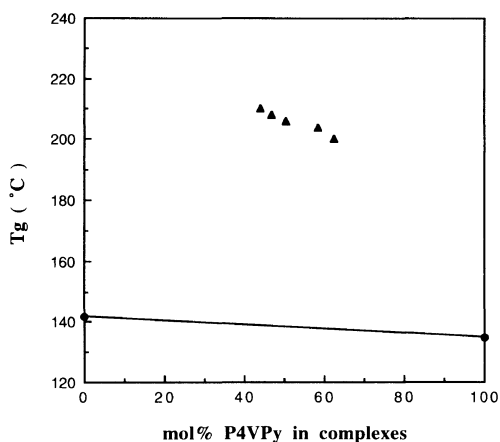
**Table I.** Experimental data of interpolymer complexes between PVPh and P2VPy or P4VPy coprecipitated from ethanol solutions

Blend systems	Feed composition		Interpolymer complexes		
	PVPy	Content	Yield	PVPy content	$T_g$
	wt%	mol%	wt%	mol%	$^\circ\text{C}$
PVPh/P2VPy	20	22	37	46	173
	40	43	62	50	169
	50	53	89	53	166
	60	63	77	55	164
	80	82	57	59	162
PVPh/P4VPy	20	22	44	44	210
	40	43	82	47	208
	50	53	90	51	206
	60	63	90	59	204
	80	82	60	62	200

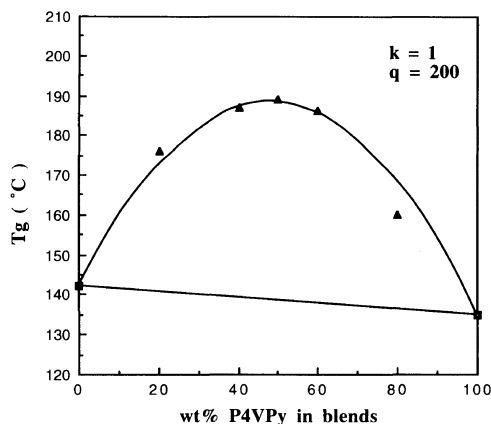


**Figure 1.**  $T_g$ -Composition relation of PVPh/P2VPy complexes obtained from ethanol solutions.

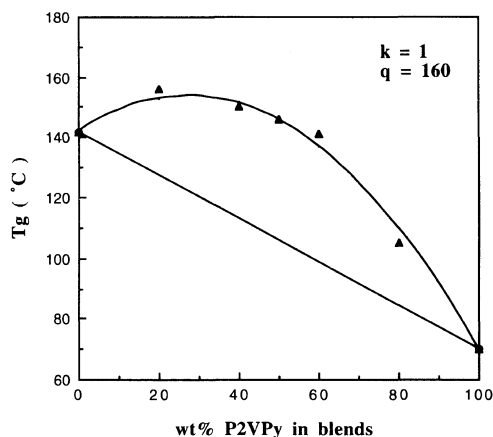
the intermolecular interaction between PVPh and P4VPy is stronger than that between PVPh and P2VPy. The compositions of the complexes, which were again basically independent of the feed compositions, varied in a narrow range centered at 50 mol% of P4VPy, suggesting the formation of 1:1 molar ratio interpolymer complexes. The  $T_g$ 's of the complexes are in the range of 200 to  $210^\circ\text{C}$  and are higher than those calculated from additivity



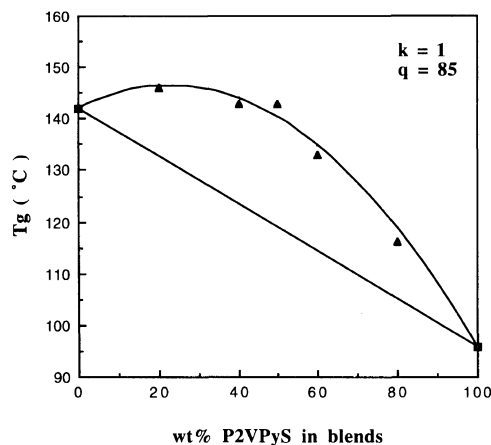
**Figure 2.**  $T_g$ -Composition relation of PVPh/P4VPy complexes obtained from ethanol solutions.



**Figure 4.**  $T_g$ -Composition curve of PVPh/P4VPy miscible blends cast from DMF solutions.



**Figure 3.**  $T_g$ -Composition curve of PVPh/P2VPy miscible blends cast from DMF solutions.



**Figure 5.**  $T_g$ -Composition curve of PVPh/P2VPyS miscible blends cast from DMF solutions.

rule by about 70°C as shown in Figure 2. The larger positive deviation in  $T_g$  values of PVPh/P4VPy complexes than that of PVPh/P2VPy complexes also indicates the stronger intermolecular interactions between PVPh and P4VPy.

Mixing the ethanol solutions of PVPh and P2VPyS gave opaque emulsion-like solutions over the entire feed compositions, from which precipitates were too little even after centrifugation to allow the determination of their compositions. This phenomenon shows that the incorporation of styrene repeating units

into P2VPy chain dilutes the concentration of pyridine groups which produces a poor complexation ability of P2VPyS with PVPh, and it in turn, indicates the important role of pyridine ring in complex formation.

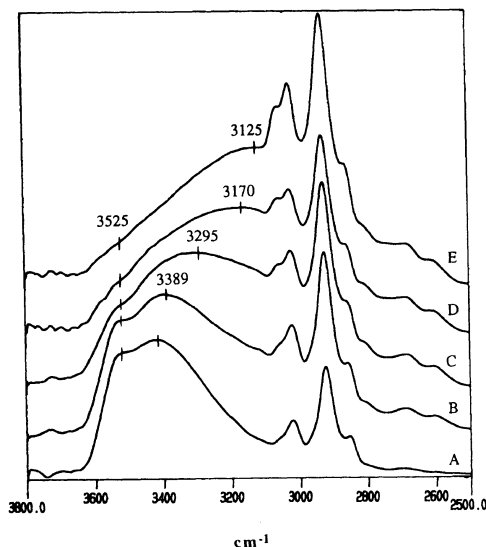
PVPh did not form interpolymer complexes with the three pyridine-containing polymers in DMF, a strong hydrogen bond breaking solvent. The  $T_g$ -composition curves of PVPh/P2VPy (Figure 3), PVPh/P4VPy (Figure 4), and PVPh/PS4VPy (Figure 5) blends cast from DMF solutions can be simulated by the Kwei equation<sup>11,12</sup>:

$$T_g(\text{blend}) = (w_1 T_{g1} + kw_2 T_{g2}) / (w_1 + kw_2) + qw_1 w_2$$

where  $k$  and  $q$  are fitting constants. The  $T_g$ 's of all the three blend systems, PVPh/P2VPy, PVPh/P4VPy and PVPh/P2VPyS, are higher than those calculated from the additivity rule, and the curves can be fitted with  $k=1$  and  $q=160$ ,  $k=1$  and  $q=200$ , and  $k=1$  and  $q=85$ , respectively. Kwei<sup>12</sup> pointed out that the quadratic term  $qw_1 w_2$  is proportional to the number of specific interactions in the blends. In this respect, the  $q$  values of the three blend systems can be used as a measure of their strength of interpolymer interactions. The results show that the relative strength of interpolymer interactions of the three pyridine-containing polymers with PVPh is in the order P4VPy > P2VPy > P2VPyS.

#### FTIR Characterization

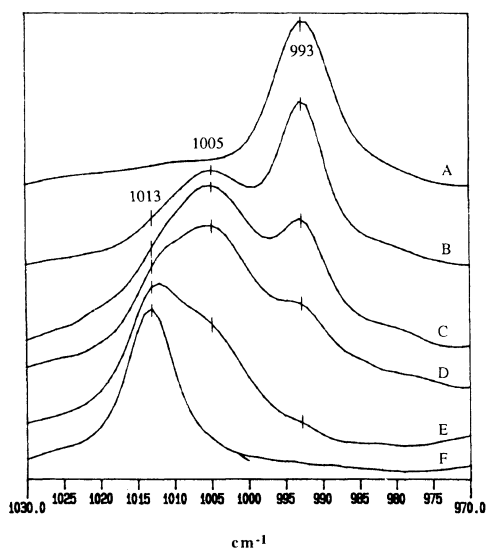
The hydroxyl stretching region in infrared spectra of the blends of PVPh/pyridine-containing polymers is sensitive to hydrogen bonding associations. Figure 6 illustrates the



**Figure 6.** FTIR spectra, recorded at 180°C, of the hydroxyl region of PVPh/P4VPy cast from DMF solutions: (A) 0; (B) 20; (C) 40; (D) 60; (E) 80 wt% P4VPy.

hydroxyl region of PVPh/P4VPy blends cast from DMF solutions and recorded at 180°C. Pure PVPh (see curve A) shows two distinct bands, a sharp band at 3525 cm<sup>-1</sup> for the absorption of free hydroxyl groups and a broad band centered at 3425 cm<sup>-1</sup> for the absorption of hydrogen bonded hydroxyl groups (self-association). Upon increasing P4VPy content in the blend, the intensity of the free hydroxyl band at 3525 cm<sup>-1</sup> decreases gradually and can not be observed when the P4VPy content in the blend reaches 60 wt%, indicating that more free hydroxyl groups are hydrogen bonded with pyridine groups as the concentration of pyridine groups is increased. On the other hand, the center of the hydrogen bonded hydroxyl band shifts to lower frequencies with increasing P4VPy content, showing the increased contribution of hydroxyl groups hydrogen bonded with pyridine groups of P4VPy. The composition dependence of the hydroxyl bands of PVPh/P2VPy and PVPh/P2VPyS blends also exhibits the same trend as of PVPh/P4VPy blends, except that the free hydroxyl bands of these two systems are still observable even when the concentration of the pyridine-containing polymers reaches 80 wt%, clearly indicative of the weaker hydrogen bonding interactions of these two systems as compared with the PVPh/P4VPy system. Coleman and co-workers have used the frequency difference between 'free' hydroxyl groups and those of the hydrogen bonded hydroxyl groups as a measure of the average strength of the intermolecular interactions.<sup>13</sup> In this respect, the average strength of the hydrogen bonds between the PVPh hydroxyl group and the pyridine nitrogen atom of the three pyridine-containing polymers are in the order of PVPh/P4VPy ( $\Delta\nu = 400 \text{ cm}^{-1}$ ) > PVPh/P2VPy ( $\Delta\nu = 390 \text{ cm}^{-1}$ ) > PVPh/P2VPyS ( $\Delta\nu = 355 \text{ cm}^{-1}$ ). The result is consistent with their interpolymer complexation behavior.

Besides the hydroxyl stretching region, some characteristic modes of the pyridine ring are



**Figure 7.** FTIR spectra, recorded at 180°C, of the region between 1030 and 970  $\text{cm}^{-1}$  of PVPh/P4VPy cast from DMF solutions: (A) 0; (B) 20; (C) 40; (D) 60; (E) 80; (F) 100 wt% PVPh.

sensitive to hydrogen bonding associations.<sup>14</sup> These modes include 1590, 1050, 993, and 625  $\text{cm}^{-1}$  and, upon forming hydrogen bonds with the carboxylic acid groups of poly(ethylene-*co*-methacrylic acid) (EMAA), are perturbed and shift to 1600, 1067, 1011, and 634  $\text{cm}^{-1}$ , respectively. Unfortunately, due to the complication of overlapping with other structure modes of the component polymer chains, only the band at 993  $\text{cm}^{-1}$  can be used to identify the existence of hydrogen bonding interactions between the pyridine groups and phenolic groups. Figure 7 shows the infrared spectra in the 970–1030  $\text{cm}^{-1}$  region of PVPh/P4VPy blends. P4VPy (see curve A) has a band at 993  $\text{cm}^{-1}$  ascribed to pyridine ring absorption; PVPh does not absorb at 993  $\text{cm}^{-1}$  but has a band at 1013  $\text{cm}^{-1}$ . The two bands are well separated and no overlap is observed. Upon the addition of PVPh to P4VPy, an absorption at 1005  $\text{cm}^{-1}$  is manifested and its relative intensity as compared with that at 993  $\text{cm}^{-1}$  for free pyridine ring increases gradually. The absorption at 1005  $\text{cm}^{-1}$ , which

is parallel to that at 1011  $\text{cm}^{-1}$  for EMAA/P2VPyS blends,<sup>14</sup> can be considered as the contribution of pyridine groups hydrogen bonded with phenolic groups. The IR spectra of PVPh/P2VPy and PVPh/P2VPyS blends also show the same trend as PVPh/P4VPy blends, thus, confirming the existence of hydrogen bonds between pyridine groups and phenolic groups.

## CONCLUSIONS

PVPh forms interpolymer complexes with P2VPy, P4VPy, and P2VPyS over the entire feed composition range in ethanol solutions, but not in DMF solutions. The complexation abilities of the three pyridine-containing polymers with PVPh in ethanol solutions were found to be in the order P4VPy > P2VPy > P2VPyS. FTIR studies show that the relative strength of hydrogen bonds between PVPh hydroxyl groups and pyridine nitrogen atoms of the three pyridine-containing polymers is also in the order P4VPy > P2VPy > P2VPyS.

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### Interpolymer Complexes of PVPh

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