

# Comparison of Specific Interactions in P4VP/PSCA and PS4VP/PSCA Blends and Complexes

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**ABSTRACT:** The compatibilization of an immiscible polymer system polystyrene/poly(4-vinylpyridine) has been induced by the introduction of carboxylic acid groups within the polystyrene chains. Poly(styrene-*co*-cinnamic acid), PSCA, copolymers were used to prepare blends and complexes with poly(4-vinylpyridine), P4VP, and in a second time with poly(styrene-*co*-4-vinylpyridine), PS4VP, copolymer in order to reduce the density of the interacting groups. The miscibility of the systems has been ascertained by DSC, which revealed that both blends and complexes exhibit a single glass transition temperature indicating their single phase nature. The  $T_g$ s of the complexes of PS4VP with PSCA15, containing 15 mol % of cinnamic acid content, were higher than those of the corresponding blends indicating that stronger interpolymer interactions were developed in the complexes. Furthermore, the appli-

cation of the Kwei equation suggested that P4VP interacts more strongly with PSCA15 than does PS4VP. FTIR spectra revealed the development of hydrogen bonding within the PS4VP/PSCA system and both hydrogen bonding and ionic interaction in the P4VP/PSCA blends whereas the same interactions were expected in both systems. This observation confirmed the stronger ability of P4VP to interact with PSCA copolymer. The viscosimetric study showed both positive and negative deviations of the reduced viscosity of the blends from the additivity law confirming the presence of specific interactions within the blend solutions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3256–3261, 2008

**Key words:** hydrogen bonding; polymer blends; FTIR; DSC; viscosimetry; glass transition; viscosity

## INTRODUCTION

Polymer blending<sup>1–3</sup> is the most commonly used way to develop new materials with specific properties. As is well known, most polymer pairs are immiscible due to the unfavorable low entropy of mixing. A considerable interest has been granted over the last decades to enhancing polymer blend miscibility by introducing functional groups capable of developing specific interactions.<sup>4–6</sup> Polymer blends study has been extended to interpolymer complexation in many recent papers. Complexes present enhanced properties that are different from those encountered in both pure components and corresponding miscible blends. Polymer complexes can be obtained by mixing polymer solutions<sup>7–10</sup>: When the polymer–polymer interactions are stronger than the polymer–solvent interactions the two polymers form precipitates which are commonly called interpolymer complexes.

Because of its lack of interacting groups polystyrene is generally immiscible with other polymers. In this article, in order to enhance the miscibility of the

polystyrene/poly(4-vinylpyridine) pair we have introduced cinnamic acid (CA) groups along the polystyrene chains capable of developing specific interactions with poly(4-vinyl pyridine) polymer. In a second time, in order to reduce the density of the interacting groups and the number of specific interactions between the antagonist chains, we decided to use the poly(styrene-*co*-4-vinylpyridine)/poly(styrene-*co*-cinnamic acid) PS4VP/PSCA system. The aim of this article is to prospect the nature and the extent of the specific interactions that occur between the 4-vinylpyridine and the CA units in both solution and bulk by using a combination of characterization techniques and to demonstrate that hydrogen bonding in PS4VP/PSCA system can be converted to an ionic interaction in P4VP/PSCA system by simply increasing the density of interacting sites.

## EXPERIMENTAL SECTION

### Polymer synthesis and characterizations

Styrene (S), and 4-vinylpyridine (4VP) were freed from inhibitor and freshly distilled under reduced pressure prior to use. CA was recrystallized from chloroform solution. PSCA containing 5, 10, 15, or 23 mol % of CA and poly(styrene-*co*-4-vinylpyridine)

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**TABLE I**  
Main Characteristics of the Polymers

Polymer	Composition (mol %)	$[\eta]$ (dL g <sup>-1</sup> )	$M_n$	$M_w$	$T_g$ (°C)
P4VP	–	–	74,400	124,400	154
PS4VP	16.61	0.65	183,700	357,800	110
PSCA5	4.70	0.61	97,100	163,300	116
PSCA10	9.97	0.52	85,000	139,200	132
PSCA15	14.70	0.40	80,500	138,300	141
PSCA23	23.20	0.34	76,600	115,300	174

PS4VP were synthesized by free radical copolymerization in dioxane and chloroform solutions respectively using one per thousand by monomers weight of 2,2'-azobisisobutyronitrile (AIBN) as initiator at 60°C, under nitrogen blanket. The conversions were kept less than 15% to prevent composition drift. The copolymers were purified by repeated dissolution/precipitation, isolated by filtration and vacuum dried at 40°C during several days. Poly(4-vinylpyridine), P4VP, polymer from PolySciences Inc. (Warrington, PA), was purified before use by dissolution/precipitation in ethanol/diethylether pair. Molecular weights were determined by SEC using a Waters GPCII. The acid content in the PSCA copolymers was determined by acid–base titration of the corresponding polymer solution in benzene/methanol (20 vol % methanol) with a standardized sodium hydroxide solution. PS4VP copolymer composition was determined from elemental analysis. The main molecular characteristics of the polymers are listed in Table I.

#### Preparation of complexes and blends

P4VP/PSCA15 blends were prepared by solvent casting from 10% (w/v) DMF solutions. Complexes were prepared by mixing 10% (w/v) butanone solutions of PS4VP and PSCA15 in different compositions. After strong agitation for 1 day to ensure thorough mixing, the precipitates were filtered and dried in vacuum at 60°C for several days. The ratio of the amount of dried complex to the total weight of two polymers in the initial solution gives the yield of the complex. The composition of the complex was determined by Elemental analysis using a Perkin–Elmer 2400 elemental analyzer. PS4VP/PSCA blends were prepared using the coprecipitation method by co-dissolving appropriate amounts of the pure components in tetrahydrofuran, a 10% (w/v) solution. The resulting solution was stirred for 1 day to ensure thorough mixing. The blend solutions were then co-precipitated in an excess of petroleum ether, isolated by filtration and washed with several portions of non-solvent. The powder samples were then vacuum dried at 60°C for several days.

#### DSC measurements

The thermal analysis was conducted on a Perkin–Elmer DSC-7 using a heating rate of 20 K min<sup>-1</sup>. The  $T_g$  was recorded as the temperature corresponding to the midpoint of the heat capacity change of the second thermal scan. All samples were preheated to 180°C and kept for 10 min at that temperature to ensure complete removal of any trace of residual solvent.

#### FTIR measurements

Infrared spectroscopic measurements were recorded on a Nicolet 560 FTIR spectrometer with a resolution of 2 cm<sup>-1</sup> and were averaged from 64 scans. The polymer blends were prepared in different weight ratios by co-dissolution of required amounts of the components in THF and DMF for PS4VP/PSCA and P4VP/PSCA systems respectively at a concentration of 1.2 g dL<sup>-1</sup>. The resulting solutions were stirred for 1 day to ensure thorough mixing and then casted onto KBr discs. The samples were dried at room temperature to reduce the evaporation rate and to avoid film cracking. After evaporation of most of the solvent, the samples were kept in a vacuum oven at 60°C for several days.

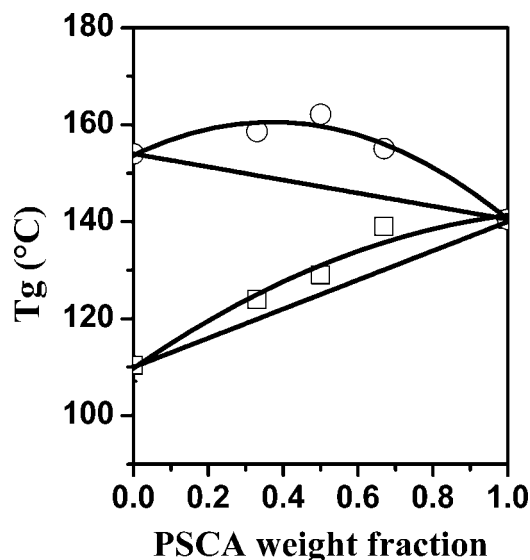
#### Viscosity measurements

Viscosity measurements were carried out using an Ubbelohde viscosimeter. Intrinsic viscosities of the different copolymers listed in Table I were determined at 25°C in THF by extrapolation to zero concentration of the plot of the reduced viscosity versus concentration.

## RESULTS AND DISCUSSION

#### Calorimetric analysis

All the DMF cast P4VP/PSCA15 blends were transparent and showed a single glass transition temperature indicating the miscibility of the system. Furthermore, the  $T_g$ s of the blends were higher than those of the pure components P4VP and PSCA15 as shown in Figure 1. This behaviour is typical of systems



**Figure 1** Plots of the experimental  $T_g$ s of the blends versus blend composition: (□) PS4VP/PSCA15, (○) P4VP/PSCA15.

developing strong specific interactions resulting in very high cross linking. PS4VP/PSCA15 blends and complexes also showed a single glass transition temperature located between those of the parent polymers and progressively moving to higher temperatures with increasing PSCA content in the blend, indicating the single-phase nature of the systems. The DSC thermograms of the PS4VP/PSCA15 blends are illustrated in Figure 2 as an example. The experimental  $T_g$  values of the P4VP/PSCA15 and PS4VP/PSCA15 blends were higher than those calculated from the additivity rule as illustrated in Figure 1. Such a positive deviation is usually observed in blends where the two components develop strong specific interactions and has been described as a result of the development of hydrogen bonding between the two polymers which reduce the mobilities of the individual chains in the blend.

Among several equations commonly used to follow the dependence of  $T_g$  on the composition of the polymer blend, the Kwei equation is the most used to describe such a positive deviation. The Kwei<sup>11</sup> equation provides an indication of the strength of specific interactions within the blend:

$$T_g = \frac{W_1 T_{g1} + KW_2 T_{g2}}{W_1 + KW_2} + qW_1 W_2 \quad (1)$$

where  $W_1$  and  $W_2$  are the weight fractions of the pure components of the blend,  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass transition temperatures of the blend and pure components 1 and 2, respectively.  $K$  and  $q$  are adjustable parameters. For systems that present strong interactions between the two polymers, such as those studied in this work,  $K$  is set equal to unity

and a simplified version of the Kwei equation is used.

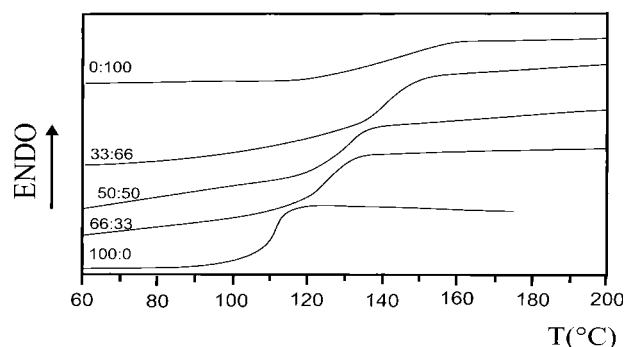
$$T_g = W_1 T_{g1} + W_2 T_{g2} + qW_1 W_2 \quad (2)$$

The parameter  $q$  has been considered as a measure of the strength of the specific interactions that are taking place between the blend components. The values of the adjustable parameter  $q$ , determined by fitting the experimental  $T_g$  data to the Kwei equation were found to be 22 and 50 for the PS4VP/PSCA15 and P4VP/PSCA15 blend systems, respectively. The larger  $q$  value obtained for the P4VP/PSCA15 system indicates that P4VP interacts more strongly with PSCA15 than PS4VP. These results suggest that as the number of the pyridine sites increases so does the intensity and/or the number of interactions within the blends.

On the other hand, as shown in Table II, the  $T_g$  values of the PS4VP/PSCA15 complexes are in the range 134–142°C. These values are higher than the  $T_g$ s of the PS4VP/PSCA15 blends having the same compositions. These higher  $T_g$ s may be attributed to the difference in structure between the complexes and the blends<sup>12–14</sup>. Although the two polymers mix randomly in a miscible blend, the antagonist chains in the complex will form pairs indicating that the strength and/or the number of the hydrogen bonds between the components in the complex are the greatest. Moreover, the compositions of the complexes are different from the feed compositions of the initial solutions. The variation of the complex  $T_g$  is in good agreement with the variation of complex composition, which depends on the composition of the original mixture. The yield of the complexes also depends on the feed composition and reaches a maximum when nearly stoichiometric amounts of PS4VP and PSCA15 were mixed.

### FTIR study

Binary blends P4VP/PSCA in the 50/50 weight ratio with different acid content in the PSCA copolymer



**Figure 2** DSC thermograms of PS4VP/PSCA15 blends (weight ratio indicated).

TABLE II  
Characteristics of the PS4VP/PSAC15 Complexes

Weight ratio in feed	Mole fraction of PSAC15 in feed	Mole fraction of PSAC15 in the complex	$T_g$ of complex ( $^{\circ}\text{C}$ )	Yield of complex (%)
80/20	0.19	0.11	134	46.4
66/33	0.32	0.37	137	70.6
50/50	0.49	0.67	138	87.2
33/66	0.65	0.58	141	79.3
20/80	0.79	0.74	142	50.9

were studied by FTIR spectroscopy. In the 1670–1570 region, Figure 3, the P4VP polymer spectrum is characterized by the  $1598\text{ cm}^{-1}$  assigned to the C=N stretching in the pyridine ring. The most remarkable feature of the blends spectra in this region is the appearance of a new band at  $1639\text{ cm}^{-1}$  which is attributed to the formation of protonated pyridine groups. The transfer of protons from the carboxylic acid groups of PSCA copolymers to the nitrogen atom of P4VP leads to the appearance of this new band, which has already been observed in blends and complexes where protonation of the pyridine groups has been observed.<sup>1,15,16</sup> This behavior for the P4VP/PSCA blends is quite different from that obtained for PS4VP/PSCA blends because no similar band has been observed for the latter system whereas the same interactions were expected in both systems. It is well established that the  $1598\text{ cm}^{-1}$  band assigned to the C=N stretching in the pyridine ring is highly affected by hydrogen bonding in both position and intensity. In the P4VP/PSCA blend spectra, the  $1598\text{ cm}^{-1}$  band is seen to shift toward high wavenumbers. This shift is readily noticeable and is not an apparent effect due to the overlapping

with the in-plane stretching mode of the styrene phenyl band which appears at  $1601\text{ cm}^{-1}$  because the overlapping with this band only, will result in a shift between 1598 and  $1601\text{ cm}^{-1}$ , depending on blend composition. Therefore, the shift to  $1604\text{ cm}^{-1}$  observed in the blends is attributable to an additional band corresponding to pyridine rings hydrogen bonded to carboxyl groups of PSCA copolymers. Furthermore, the contribution of the pyridinium ion band at  $1639\text{ cm}^{-1}$  decreases at the expense of the hydrogen bonding band at  $1604\text{ cm}^{-1}$  as the CA content is raised in the PSCA copolymer. This result suggests that the extent of protonation of the pyridine units is limited and that not all the acid groups will be involved in an ionic interaction.

Figure 4 shows the FTIR spectra in the hydroxyl region of PSCA15 and PS4VP/PSCA15 blend in the 50/50 weight ratio, as a typical example, because all blend spectra fit the same general profile regardless of blend composition. The spectrum of the PSCA15 shows a broad band that extends over the  $3600\text{--}2400\text{ cm}^{-1}$  range with a maximum at about  $3000\text{ cm}^{-1}$ , assigned to self-associated hydrogen bonded acid groups in cyclic structures or dimeric form. The other characteristic band of self associated dimeric

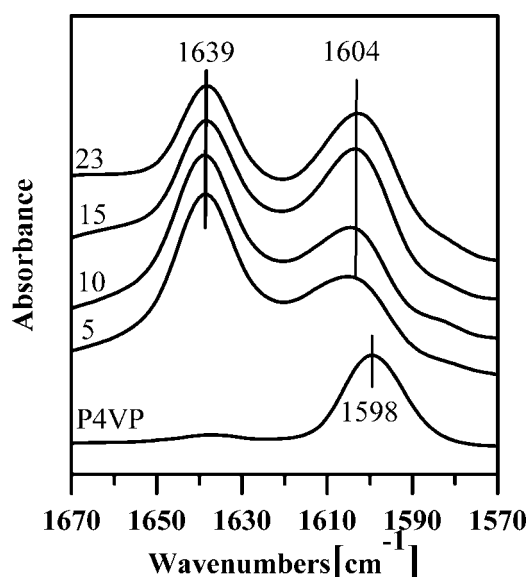


Figure 3 FTIR spectra of the P4VP/PSCA blends in the 50/50 weight ratio in the  $1670\text{--}1570\text{ cm}^{-1}$  region (CA content in the PSCA copolymer indicated).

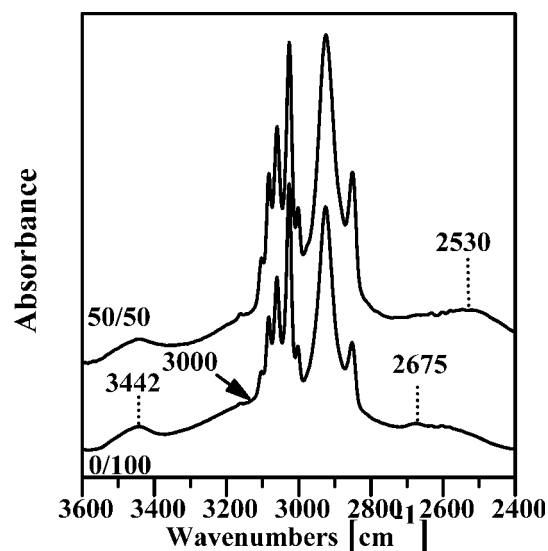


Figure 4 FTIR spectra of PSCA15 and the 50/50 PS4VP/PSCA15 blend in the hydroxyl region.

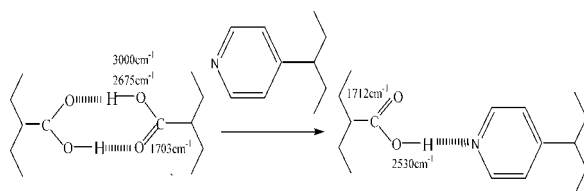
groups is the broad band at about  $2675\text{ cm}^{-1}$ , a satellite band enhanced by Fermi resonance. Moreover, a weak band observed at  $3442\text{ cm}^{-1}$  is attributed to the carboxylic acid units that are intermolecularly hydrogen bonded to the  $\pi$  system of the phenyl groups in the PSCA copolymers.<sup>17,18</sup> In this region we can also observe the aliphatic and aromatic C—H stretching bands between  $3100$  and  $2800\text{ cm}^{-1}$ . In the PS4VP/PSCA15 blend spectrum the satellite band initially centred at  $2675\text{ cm}^{-1}$  in the PSCA15 spectrum shifts considerably to lower frequencies at  $2530\text{ cm}^{-1}$  in the 50/50 blend ratio. This shift suggests that the introduction of the PS4VP16 content in the blend disrupts some of the cyclic self-associated dimeric carboxylic acid groups in favor of their association via hydrogen bonding with the 4-vinylpyridine groups of PS4VP as demonstrated in Scheme 1.

Furthermore, the frequency shift of the satellite band to lower wavenumbers ( $\Delta\nu = 145\text{ cm}^{-1}$ ) is considerable and demonstrates that the new interaction between the proton of the carboxylic acid groups and the nitrogen of the 4-vinylpyridine groups is stronger than the acid self-association in pure PSCA15.

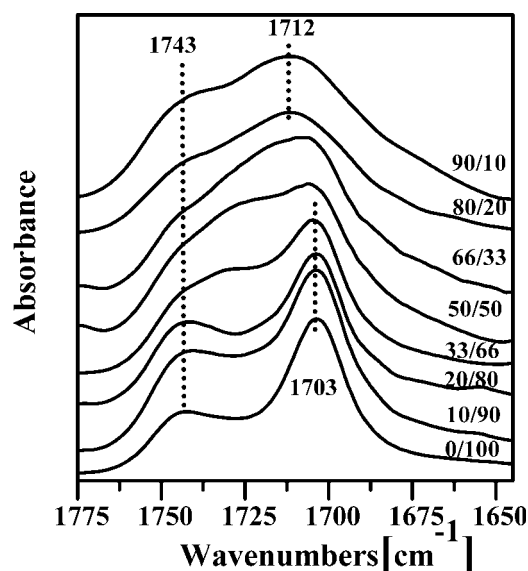
In the carbonyl region, Figure 5, the PSCA15 copolymer spectrum is dominated by the characteristic band of self association attributed to the carboxylic acid dimers at  $1703\text{ cm}^{-1}$ . The band at  $1743\text{ cm}^{-1}$  is assigned to the free C=O carbonyl groups. In the PS4VP/PSCA15 blends, although the appearance of a distinct band cannot be detected at first sight in the blend spectra, the broadening observed between the two bands at  $1703\text{ cm}^{-1}$  and  $1743\text{ cm}^{-1}$  of the PSCA15 spectrum suggests the presence of a new contribution corresponding to the carbonyl groups of the acidic copolymer associated with the pyridine groups of PS4VP. This new band can be readily located at  $1712\text{ cm}^{-1}$  for blend compositions with high PS4VP content.

### Viscosimetry study

In this article, the variation of the reduced viscosity versus blend composition has been used to prospect the formation of interpolymer interactions in solution. It is well established<sup>19</sup> that in the absence of specific interactions, the reduced viscosity of dilute polymer blend solution is often close to the weight average reduced viscosities of the blend components. Indeed, in dilute solutions which are characterized

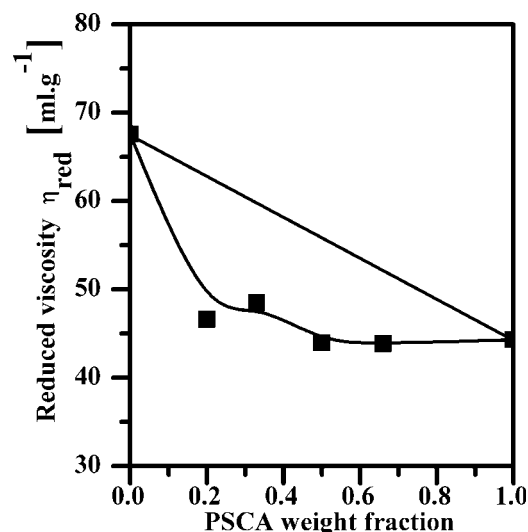


**Scheme 1** Schematic diagram of cinnamic acid/4-vinylpyridine hydrogen bonding interaction.

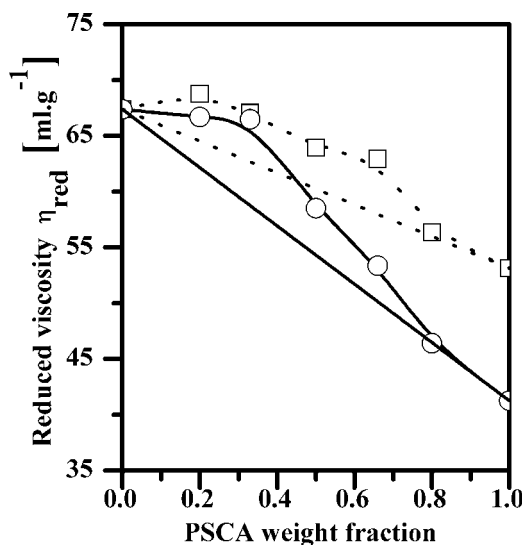


**Figure 5** FTIR spectra of the PS4VP/PSCA15 system in the carbonyl region (weight ratio indicated).

by a concentration less than the critical concentration ( $C < C^*$ ) the polymer chains exist as separated coils in absence of specific interactions. Positive or negative deviation of the reduced viscosities of the blends from the additivity law will be then an indication of the presence of specific interactions within the blend solutions.<sup>19,20</sup> In this study, a total concentration of  $0.15\text{ g dL}^{-1}$  corresponding to a much lower concentration than the critical concentration  $C^*$  calculated as  $C^* = 1/[\eta]$ , was used to prospect the presence of specific interactions in solution between the antagonist chains. In both THF and DMF the polymer solutions were clear indicating that no complex can be formed in these solvents.



**Figure 6** Reduced viscosity as a function of blend composition of P4VP/PSCA15 in DMF.



**Figure 7** Reduced viscosity as a function of blend composition of (□) PS4VP/PSCA10, (○) PS4VP/PSCA15 in THF.

A plot of the reduced viscosity as a function of blend composition for P4VP/PSCA15 solutions in DMF is reported in Figure 6. As can be seen the reduced viscosities of the blend solutions are significantly lower than the values calculated by the additivity law:

$$\eta_r = W_1 \cdot \eta_{r1} + W_2 \cdot \eta_{r2}$$

where  $W_1$ ,  $W_2$  are the weight fractions of the pure components of the blend,  $\eta_r$ ,  $\eta_{r1}$  and  $\eta_{r2}$  are the reduced viscosities of the blend and pure components 1 and 2, respectively.

This behaviour indicates that the associations within the P4VP/PSCA15 blend solutions are so strong that a contraction of the components polymer chains is observed and results in a viscosity decrease. This result is in good agreement with the DSC results, which revealed that the intermolecular interactions in the P4VP/PSCA blends were so strong that the  $T_g$  values of the blends were raised up to the  $T_g$ s of the individual components.

Figure 7 shows the variation of the reduced viscosity as a function of blend composition for PS4VP/PSCA10 and PS4VP/PSCA15 in THF. The reduced viscosities of blend solution are higher than those calculated from the additivity rule. This positive deviation is obviously an indication of the presence of intermolecular interactions between the PS4VP and PSCA15 chains in solutions. The difference in viscosity behavior between the PS4VP/PSCA and P4VP/PSCA systems can be attributed to the difference in the association structure of the antagonist chains in the different systems.

## CONCLUSIONS

In this study, the appearance of a single  $T_g$  in P4VP/PSCA15 blends and PS4VP/PSCA15 blends and

complexes indicates the single-phase nature of the different systems. The large positive deviation of the  $T_g$ s of the blends and complexes from the additivity law suggests that the interactions within the binary blends and complexes are strong. Furthermore, the  $T_g$  values of the PS4VP/PSCA15 complexes are higher than those of the corresponding blends having the same compositions indicating stronger interactions in the complexes. The thermal analysis shows again that P4VP interacts more strongly with PSCA15 than PS4VP but does not distinguish between hydrogen bonding and ionic interaction in the studied systems. The FTIR study reveals the existence of hydrogen bonding in both P4VP/PSCA and PS4VP/PSCA systems and partial protonation of the pyridine units in the P4VP/PSCA blends. The viscosimetric study further indicates the presence of strong interpolymer interactions in solution. Although the viscosimetric study was carried out in DMF or THF where interactions may be totally or partially hindered by the presence of the solvent molecules, which compete with the basic copolymer to hydrogen bond with the PSCA chains preventing interpolymer interaction formation, deviations of the reduced viscosity of the blend solution from the additivity law were observed in both solvents.

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