

# Blends Containing Amphiphilic Polymers. V. Compatibilization of *N*-Alkylitaconamic Acid-*co*-Styrene Copolymers with Interacting Polymers

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**ABSTRACT:** The phase behavior of blends containing *N*-alkylitaconamic acid-*co*-styrene copolymers (NAIA-*co*-S) with poly(*N*-vinyl-2-pyrrolidone) (PVP) of two different weight average molecular weights ( $\overline{M}_w$ ), poly(2-vinylpyridine) (P2VPy) and poly(4-vinylpyridine) (P4VPy), was analyzed by differential scanning calorimetry and Fourier transform infrared spectroscopy. Copolymers containing 80% S are miscible with PVP<sub>10</sub>, PVP<sub>24</sub>, and P4VPy over the whole range of composition. In the case of blends with P2VPy, miscibility is observed only for the first three members of the series, i.e., NEIA-*co*-S, NPJA-*co*-S, and NBIA-*co*-S. For copolymers containing hexyl to dodecyl moieties, phase separation is observed in blends with P2VPy. Copolymers containing 50% S are miscible over the whole range of composition irrespective of the homopolymer and the length of the side chain of

the itaconamic moiety of the copolymer. This behavior is interpreted in terms of steric hindrance, in the sense that the copolymers with long side chains are not able to interact with the nitrogen of P2VPy because of the position in the aromatic ring. The interactions between copolymers and homopolymers are discussed in terms of specific interactions like hydrogen bonds between the itaconamic moiety and the different functional groups of the homopolymers, together with the hydrophobic interaction, which cannot be disregarded. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2512–2519, 2006

**Key words:** amphiphilic polymers; *N*-1-alkylitaconamic acid-*co*-styrene copolymer; DSC; FTIR; compatibility; hydrogen bonds; hydrophobic effect

## INTRODUCTION

Much attention has been paid in recent years to the characterization of polymer blends. The increasing interest is mainly because polymer blending is a common and potentially versatile method of developing new materials with designed properties, which cannot be achieved by using single polymers.<sup>1,2</sup> Polymer blends have been used widely, since they often have physical properties superior to the component polymers<sup>3</sup>; however, the development of new useful blends is severely limited by the incompatibility of many polymer pairs of interest.<sup>4</sup> Because the gain in combinatorial entropy upon mixing two high-molecular weight polymers is very small, miscibility of polymer pairs is most often

the result of an exothermic heat of mixing.<sup>5,6</sup> Specific interactions as well as the dilution of repulsive interactions by less unfavorable ones can produce negative heat of mixing.<sup>6,7</sup> The role of polymer–polymer interactions in determining the phase behavior and final properties of polymer blend materials is of interest in the prediction of miscibility in polymer blends.<sup>7–10</sup> However, the occurrence of stable single-phase polymer blends is not restricted to systems in which miscibility derives from specific interpolymer interactions. A significant number of systems in which at least one component is a random copolymer show miscibility over a range of copolymer composition, even though combinations of the corresponding homopolymers are immiscible.<sup>11</sup> The origin of miscibility in such systems is proposed to be the so-called “repulsion effect” between the covalently bonded comonomer units of the copolymer.<sup>11–13</sup> Compatibility in multifunctional polymers is in general favored by specific interactions such as hydrogen bonding, dipole–dipole interactions, acid–base interactions, or complexation between the components.<sup>14–16</sup> These interactions give rise to negative heat of mixture, favoring mixing process. In previous works, the blending process of poly(*N*-1-alkylitaconamic acids)

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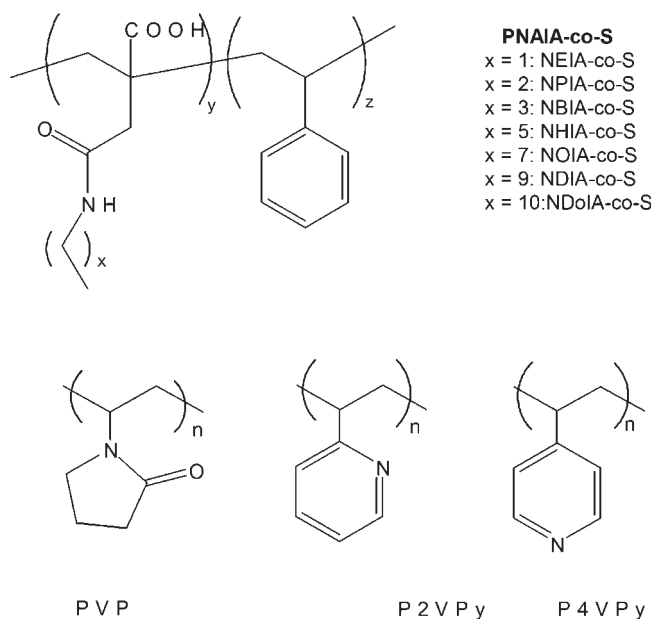
(PNAIA) with different homopolymers have been reported,<sup>15,16</sup> and the effect of specific interactions such as hydrogen bonding formation was analyzed. The combination of functionalized copolymers with different interacting homopolymers should be interesting to promote miscibility or miscibility windows in phase-separated systems. In fact, on one hand, specific interactions would favor intermolecular segment–segment interactions and, on the other hand, the presence of a copolymer would condition the miscibility due to repulsive effect in combined systems.

The aim of the present work is to analyze the miscibility behavior of (*N*-1-alkyl itaconamic acids-*co*-styrene) (NAIA-*co*-S) copolymers, containing different long side chains in the itaconamic moiety, i.e., ethyl (NEIA-*co*-S), propyl (NPIA-*co*-S), butyl (NBIA-*co*-S), hexyl (NHIA-*co*-S), octyl (NOIA-*co*-S), decyl (NDIA-*co*-S), and dodecyl (NDoIA-*co*-S), with several interacting homopolymers such as poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(2-vinylpyridine) (P2VPy), and poly(4-vinylpyridine) (P4VPy) (Scheme 1). Calorimetric and Fourier transform infrared (FTIR) studies of the blends should be the appropriate tools to describe the phase behavior of these combinations of blends.

## EXPERIMENTAL

### Monomers and polymers

*N*-1-Alkylitaconamic acids (NAIA) were synthesized by the reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform, following procedures previously reported and improved by us.<sup>15–18</sup>



**Scheme 1** Chemical structure of (itaconamic acid-*co*-styrene) copolymers, poly(vinylpyrrolidone), poly(2-vinylpyridine), and poly(4vinylpyridine).

Copolymerization of the monomers with styrene was carried out by radical polymerization in bulk at 354–388 K (depending on the NAIA used) under nitrogen, using  $\alpha,\alpha'$ -azobisisobutyronitrile (0.6% mol) as initiator. The conversion of most of the copolymers were rather low (<10%) as previously reported.<sup>17</sup> Purification of the copolymers was achieved by reprecipitation with methanol in a THF solution, before vacuum drying. Poly(*N*-vinyl-2-pyrrolidone) of two weight average molecular weight  $\overline{M}_w = 10,000$  and  $\overline{M}_w = 24,000$  (PVP<sub>10</sub> and PVP<sub>24</sub>, respectively), poly(2-vinylpyridine) (P2VPy) with  $\overline{M}_w = 37,500$ , and poly(4-vinylpyridine) (P4VPy) with  $\overline{M}_w = 50,000$  were used. Copolymers were characterized by <sup>1</sup>H-NMR in a Bruker AC-200 spectrometer, using TMS as an internal standard and deuterium oxide as solvent.

### Preparation of the blends

Blends of different compositions were prepared by solution-casting, using THF as solvent, and then evaporated at room temperature and vacuum-dried at 298 K for 120 h. The polymer concentration in the solution was about 2% w/w.

### DSC measurements

The glass transition temperatures ( $T_g$ ) of the pure polymers and blends were measured with a Mettler TA-3000 system equipped with a TC-10A processor and a differential scanning calorimeter (DSC)-20 cell and a Mettler 821 calorimetric system, using the STARE program. Polymer samples were dried under reduced pressure in a vacuum oven, prior to measurements. Dry nitrogen was used as purge gas, and thermograms were measured in the range 308–523 K at a scan rate of 20° min<sup>-1</sup>.

### FTIR measurements

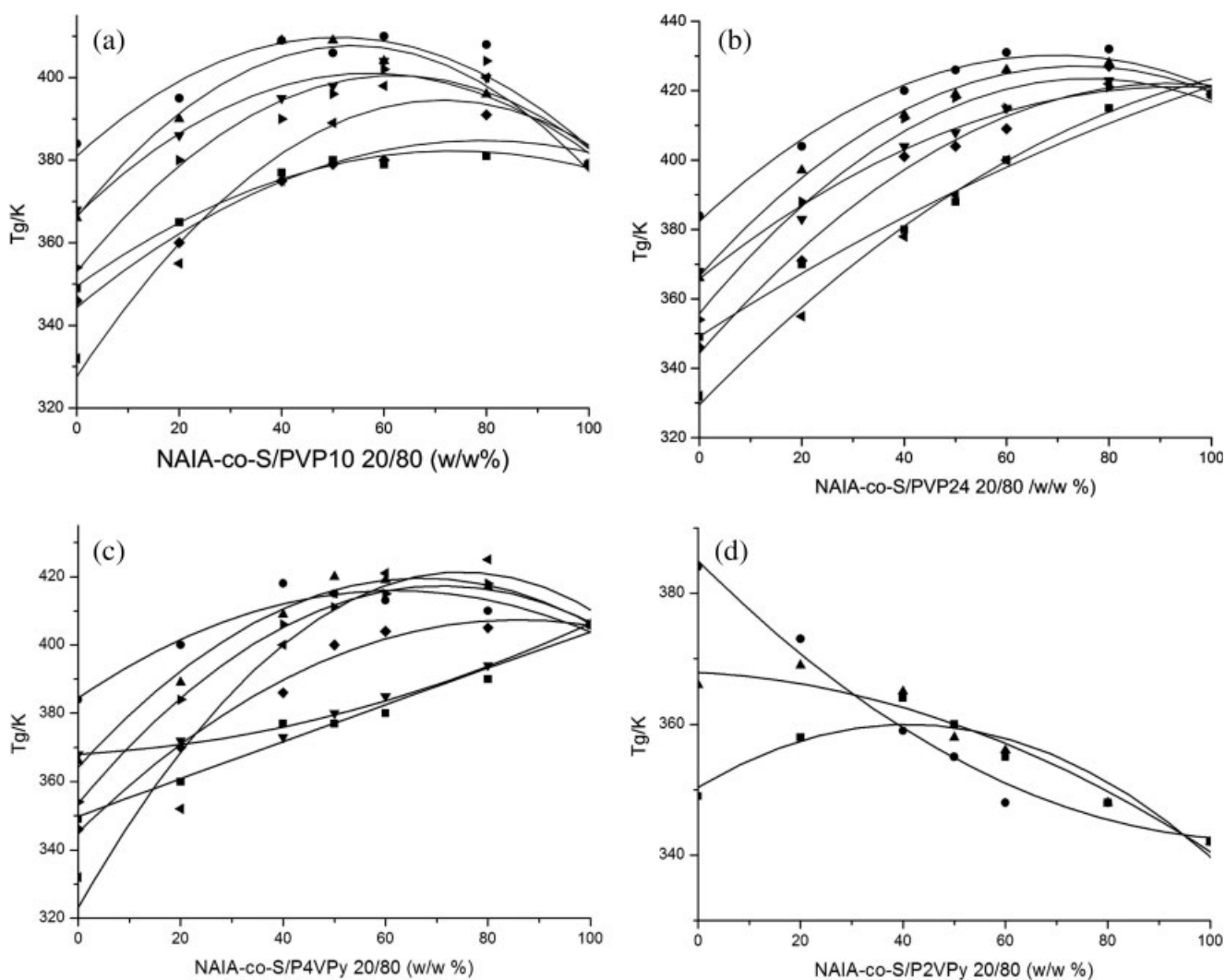
Infrared spectra of pure polymers and blends were recorded on a Vector 22 Bruker FTIR spectrophotometer. The spectra were recorded with a resolution of 1 cm<sup>-1</sup>. The samples were prepared directly in KBr pellets. Composition of the copolymers were determined by elementary analysis measurements, following the nitrogen content in the copolymer.

## RESULTS AND DISCUSSION

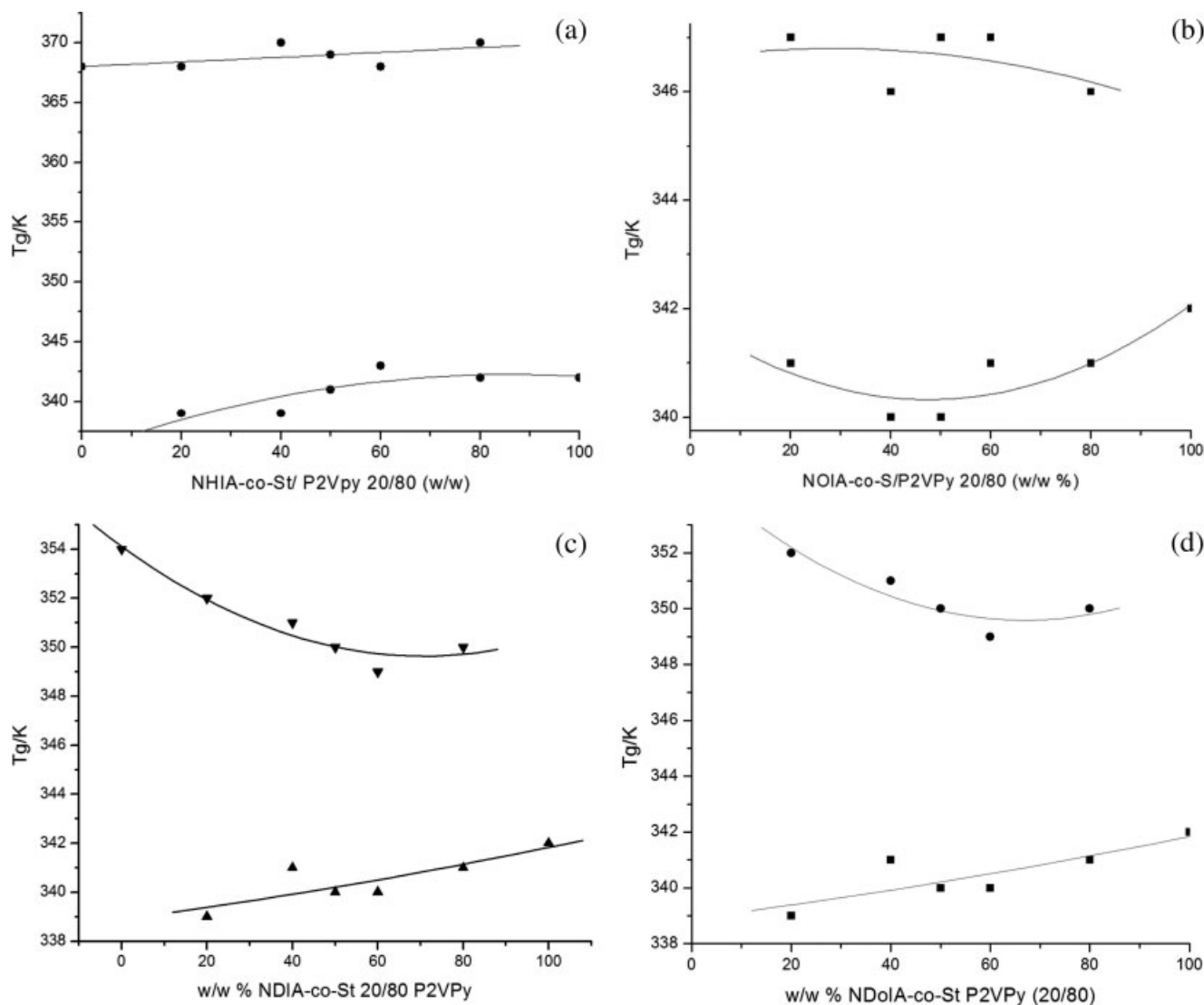
Copolymers of NAIA (PNAIA-*co*-S), i.e., NEIA-*co*-S, NPIA-*co*-S, NBIA-*co*-S, NHIA-*co*-S, NOIA-*co*-S, NDIA-*co*-S, and NDoIA-*co*-S of two different copolymer compositions (80 and 50% of styrene), were selected for the present study. PVP of two weight average molecular weight  $\overline{M}_w = 10,000$  PVP<sub>10</sub>, and 24,000 PVP<sub>24</sub>, P2VPy with  $\overline{M}_w = 37,500$  and P4VPy with  $\overline{M}_w = 50,000$  were

blended with each one of the PNAIA under study, in the whole range of blend compositions. The DSC thermograms of the films containing dry blends of NEIA-*co*-S, NPIA-*co*-S, NBIA-*co*-S, NHIA-*co*-S, NOIA-*co*-S, NDIA-*co*-S, and NDoIA-*co*-S of 80% styrene copolymer composition with PVP<sub>10</sub>, PVP<sub>24</sub>, P2VPy, and P4VPy at different compositions show distinct single glass transition temperatures ( $T_g$ ). Transparent films of the blends containing PVP<sub>10</sub>, PVP<sub>24</sub>, and P4VPy, in all cases, show  $T_g$  values intermediate to those of the pure components. Figure 1(a–c) represents the variation of  $T_g$  with the blend composition for these systems containing copolymers with 80% styrene with PVP<sub>10</sub>, PVP<sub>24</sub>, and P4VPy. For blends containing P2VPy, one single  $T_g$  and transparent films are observed only for the first three members of the series of copolymers, i.e., NEIA-*co*-S, NPIA-*co*-S, and NBIA-*co*-S. [Fig. 1(d)].

From hexyl to dodecyl derivatives, blends containing P2VPy show cloudy films and two  $T_g$  values are observed that correspond to that of the pure components; in these cases, phase separation takes place. Figure 2 shows the two  $T_g$  observed in these systems. The results shown in Figure 1, as a first approach, would be indicative of one-phase material and, therefore, miscibility over the whole range of compositions for the systems studied. The phase separation in blends containing P2VPy, shown in Figure 2, could be attributed to immiscibility due to the steric hindrance that unfavour the interaction between the carboxylic or amido groups of PNAIA with the nitrogen in P2VPy. In fact, as the side chain of the itaconamic moiety increases, the volume and steric hindrance increases and, therefore, the interaction through the nitrogen in position 2 of the aromatic ring is strongly hindered.



**Figure 1** Phase diagrams— $T_g$  vs. composition for blends of NAIA-*co*-S 20/80 w/w % with PVP<sub>10</sub>, PVP<sub>24</sub>, P2VPy, and P4VPy. (a) PVP<sub>10</sub>: (●) NEIA-*co*-S, (■) PNPIA-*co*-S, (▲) PNBIA-*co*-S, (▼) PNHIA-*co*-S, (◆) PNOIA-*co*-S, (◄) PNDIA-*co*-S, and (►) PNDDoIA-*co*-S. (b) PVP<sub>24</sub>: (●) NEIA-*co*-S, (■) PNPIA-*co*-S, (▲) PNBIA-*co*-S, (▼) PNHIA-*co*-S, (◆) PNOIA-*co*-S, (◄) PNDIA-*co*-S, and (►) PNDDoIA-*co*-S. (c) P4VPy: (●) NEIA-*co*-S, (■) PNPIA-*co*-S, (▲) PNBIA-*co*-S, (▼) PNHIA-*co*-S, (◆) PNOIA-*co*-S, (◄) PNDIA-*co*-S, and (►) PNDDoIA-*co*-S. (d) P2VPy (●) NEIA-*co*-S, (■) PNPIA-*co*-S, and (▲) PNBIA-*co*-S.

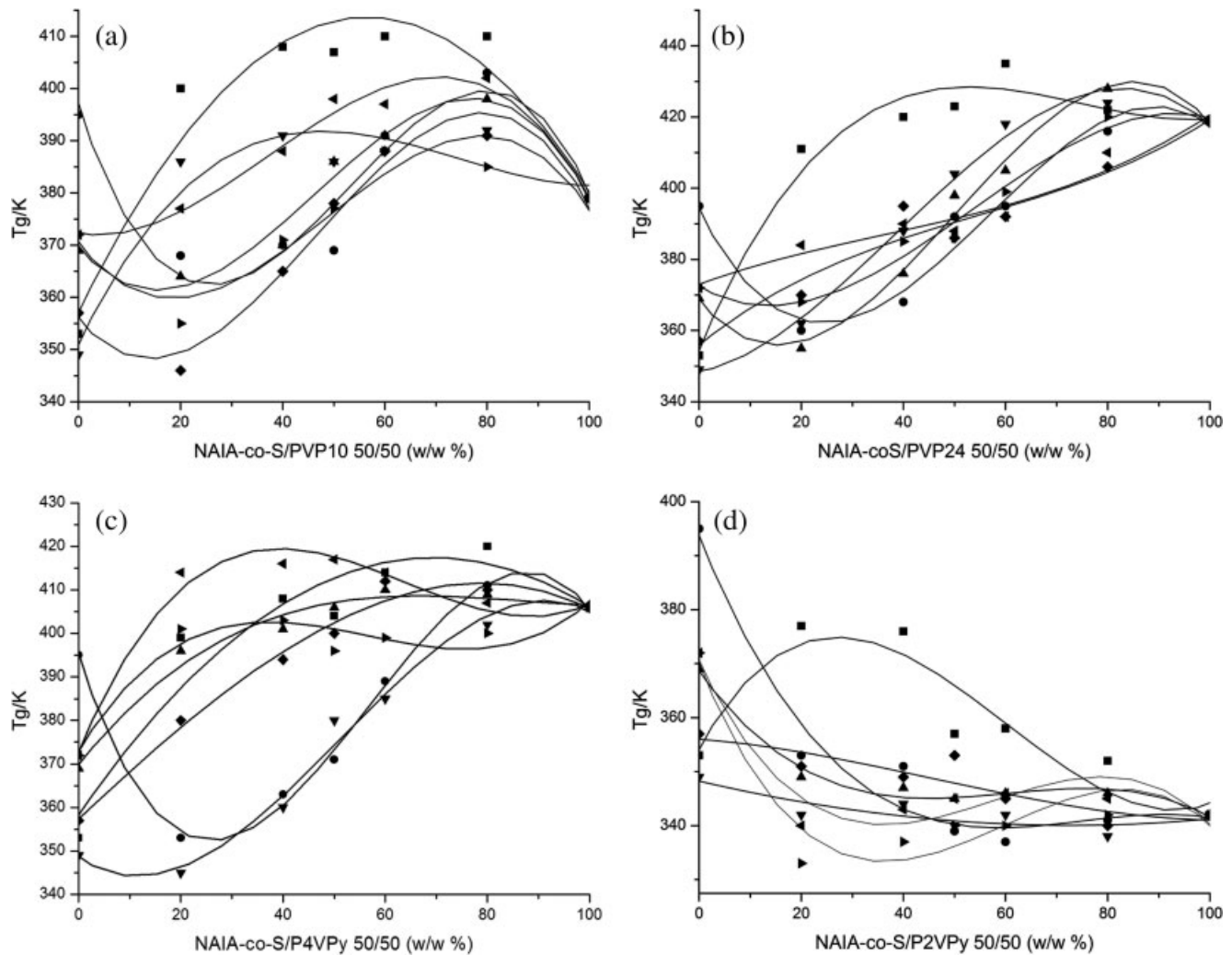


**Figure 2** Phase diagrams— $T_g$  vs. composition for blends of P2Vpy with (■) NHIA-*co*-S, (●) NOIA-*co*-S, (▲) NDIA-*co*-S, and (◆) NdoIA-*co*-S.

Figure 3 shows the phase diagrams for blends of NEIA-*co*-S, NPIA-*co*-S, NBIA-*co*-S, NHIA-*co*-S, NOIA-*co*-S, NDIA-*co*-S, and NDoIA-*co*-S of 50% styrene copolymer composition, with PVP<sub>10</sub>, PVP<sub>24</sub>, P2Vpy, and P4Vpy at different compositions. As can be observed, all the blends show only one single  $T_g$  value that is indicative that they are miscible over the whole range of composition, irrespective of the homopolymer and the length of the side chain of the itaconamic moiety. This is a very important difference between the copolymers of 80 and 50% styrene composition. As the copolymer composition increases in PNAIA, the miscibility with the four homopolymers increases. This result could be explained taken into account that for the copolymers with 50% composition the amount of interacting itaconamic groups has been increased; therefore, there is a larger probability of interaction. On the other hand, in the case of blends with NAIA-*co*-S 50% S, the strength

of the interaction diminishes as the length of the side chain increases. However, this variation is not too drastic and can be attributed to the fact that the interaction diminishes as the length of the chain increases, and the hydrophobicity of the chain also increases. Therefore, the interaction process in these systems should be a kind of balance between specific interactions that are unfavored as the steric hindrance increases, but is compensated by the hydrophobic interaction.

There are differences in the shape of the curves of Figures 1 and 3, and the degree of curvature is rather different among the blends. According to the experimental results previously reported for different kinds of miscible polymer blends, the degree of concavity in the  $T_g$ -composition plots can be considered as inversely proportional to the strength of the interaction between the two polymers in the blend.<sup>18,19</sup> The concavity in the  $T_g$ -composition plots is observed even



**Figure 3** Phase diagrams— $T_g$  vs. composition for blends of NAIA-co-S 50/50 w/w % with PVP<sub>10</sub>, PVP<sub>24</sub>, P2VPy, and P4VPy. (a) PVP<sub>10</sub>: (●) NEIA-co-S, (■) PNPIA-co-S, (▲) PNBIA-co-S, (▼) PNHIA-co-S, (◆) PNOIA-co-S, (◄) PNDIA-co-S, and (►) PNDoIA-co-S. (b) PVP<sub>24</sub>: (●) NEIA-co-S, (■) PNPIA-co-S, (▲) PNBIA-co-S, (▼) PNHIA-co-S, (◆) PNOIA-co-S, (◄) PNDIA-co-S, and (►) PNDoIA-co-S. (c) P4VPy: (●) NEIA-co-S, (■) PNPIA-co-S, (▲) PNBIA-co-S, (▼) PNHIA-co-S, (◆) PNOIA-co-S, (◄) PNDIA-co-S, and (►) PNDoIA-co-S. (d) P2VPy: (●) NEIA-co-S, (■) PNPIA-co-S, (▲) PNBIA-co-S, (▼) PNHIA-co-S, (◆) PNOIA-co-S, (◄) PNDIA-co-S, and (►) PNDoIA-co-S.

in polymer–polymer blends that present strong interactions.<sup>2,20–24</sup>

To analyze in a quantitative way the variation of  $T_g$  with the blend composition, the Gordon Taylor (GT) and Couchman (Cou) treatment of the data was used. GT and Cou equations dealing with these procedures are expressed, respectively, as follows:

$$T_g = \frac{w_1 T_{g1} + w_2 T_{g2}}{w_1 + k_1 w_2} \quad (1)$$

$$\ln T_g = \frac{\ln T_{g1} + \left(\frac{k_2 w_2}{w_1}\right) \ln T_{g2}}{1 + \left(\frac{k_2 w_2}{w_1}\right)} \quad (2)$$

where  $T_g$  is the glass transition of the blend and  $T_{gi}$  are the  $T_{gs}$  of the pure components, and  $w_1$  and  $w_2$

the weight fractions of the components of the blend. The analysis of the degree of interaction between the components of the blend can be carried out by comparison of the  $k_{GT}$  and  $k_{cou}$  parameters for the different systems studied. According to the experimental results previously reported for different kind of miscible polymer blends, the degree of concavity in the  $T_g$ –composition plots can be considered as inversely proportional to the strength of the interaction between the two polymers in the mixture.<sup>19</sup>

From this procedure, it is possible to estimate the strength of the interaction through the knowledge of the  $k_i$ , i.e.,  $k_{GT}$  and  $k_{cou}$  values of both equations.

Table I compiles the GT and Cou constants,  $k_{GT}$  and  $k_{cou}$ , for the systems studied. These parameters can be considered as a semiquantitative measure of the strength of the interaction of the blends as Belorgey and

TABLE I  
Gordon Taylor ( $k_{GT}$ ) and Couchman ( $k_{cou}$ ) Constants for the Blends of PNAIA with PVP<sub>10</sub>, PVP<sub>24</sub>, P2VPy, and P4VPy

	PVP <sub>10</sub>		PVP <sub>24</sub>		P2VPy		P4VPy	
	$k_{GT}$	$k_{Cou}$	$k_{GT}$	$k_{Cou}$	$k_{GT}$	$k_{cou}$	$k_{GT}$	$k_{Cou}$
NAIA- <i>co</i> -S (80% S)								
NEIA- <i>co</i> -S	0.05	0.05	0.50	0.49	0.23	0.23	0.20	0.19
NPIA- <i>co</i> -S	0.03	0.04	0.03	0.03	0.09	0.11	0.01	0.05
NBIA- <i>co</i> -S	0.01	0.02	0.01	0.02	0.66	0.70	0.28	0.30
NHIA- <i>co</i> -S	0.20	0.20	0.36	0.40	0.19	0.21	0.30	0.30
NOIA- <i>co</i> -S	0.34	0.35	0.51	0.50	0.04	0.04	0.38	0.40
NDIA- <i>co</i> -S	0.19	0.39	1.00	0.10	0.16	0.18	0.79	0.80
NDoIA- <i>co</i> -S	0.22	0.40	0.25	0.28	0.14	0.15	0.86	0.84
NAIA- <i>co</i> -S (50% S)								
NEIA- <i>co</i> -S	0.05	0.04	0.04	0.04	0.25	0.25	0.02	0.02
NPIA- <i>co</i> -S	0.26	0.27	0.04	0.04	0.25	0.25	0.02	0.02
NBIA- <i>co</i> -S	0.26	0.27	0.24	0.25	0.10	0.11	0.66	0.67
NHIA- <i>co</i> -S	0.15	0.15	0.88	0.86	0.25	0.23	0.18	0.15
NOIA- <i>co</i> -S	0.55	0.54	0.58	0.59	0.25	0.23	0.20	0.20
NDIA- <i>co</i> -S	0.67	0.68	0.40	0.42	0.75	0.76	0.05	0.06
NDoIA- <i>co</i> -St	0.34	0.35	0.46	0.47	0.54	0.55	0.12	0.13

Prud'homme pointed out.<sup>19</sup> The concavity of the  $T_g$ -composition plots is observed even in polymer-polymer blends that present strong interactions.<sup>20-25</sup> The results shown in Table I indicate that stronger interactions take place when the copolymer composition is of 50% styrene. The interactions when the copolymer composition is 80% S are important, but only for the first three members of the series. Nevertheless, this is not valid for all the blend compositions. However, clearly the values of  $k_{GT}$  and  $k_{Cou}$  are higher for blends containing P2VPy. Another interesting result is that as the length of the side chain of NAIA increases the interaction diminishes that can be attributed to some steric hindrance due to the long hydrophobic chain, but the diminishing is not enough to produce a phase separation that can be attributed to certain contribution of the hydrophobic effect. However, the interaction should be minor as the steric hindrance increases, but the hydrophobic interaction of the long side chains gives rise to a kind of competition and, therefore, the interaction between the components remains and miscibility is observed.

To obtain further information about the interactions involved in the mixing process, FTIR measurements were performed. Depending on the functional group analyzed, i.e., acidic carbonyl at 1775  $\text{cm}^{-1}$ , amidic carbonyl at 1700  $\text{cm}^{-1}$ , NH group at 3450  $\text{cm}^{-1}$ , the carbonyl group of PVP at 1655  $\text{cm}^{-1}$ , and the aromatic ring in the case of P2VPy at 750  $\text{cm}^{-1}$  and P4VPy at 820  $\text{cm}^{-1}$  and the composition of the copolymer, it can be observed as an important shift in FTIR. In fact FTIR spectra for blends containing NAIA-*co*-S 80% show shifts from 7 to 11  $\text{cm}^{-1}$  for blends containing PVP<sub>10</sub>, PVP<sub>24</sub>, and P4VPy. For blends containing P2VPy, this behavior is observed only for the first three members of the series of copolymers. No shift is observed or at least 1–2  $\text{cm}^{-1}$  for blends containing hexyl to dodecyl substituents in the copolymer. In the case of copolymers

containing 50% S, all the systems, except for blends containing P2VPy, show significative displacements of the bands in the FTIR spectra. Table II summarizes the displacements observed for blends of NAIA-*co*-S 50% with PVP<sub>10</sub>, PVP<sub>24</sub>, P2VPy, and P4VPy at different blend compositions. In this Table, the blends with the copolymer containing 50% S are included as an example of the general behavior. This result is in good agreement with the calorimetric one in the sense that, for the three first members of the series, interaction between the components takes place and one phase material is observed. For blends containing P2VPy, the displacements of the bands in general are small.

For blends containing NAIA-*co*-S 50% S, the behavior is quite different in the sense that important displacements of the bands are observed irrespective of the polymer studied. This is also a result in agreement with the calorimetric ones. In fact, as the copolymer composition increases in NAIA, (50% S) there are a larger number of amide and carboxylic groups to interact with the homopolymers. In this case, the hydrophobic effect described earlier is also observed and, therefore, this hydrophobic interaction cannot be disregarded.

## CONCLUSIONS

Blends containing NAIA-*co*-S with 80% S are miscible over the whole range of composition with PVP<sub>10</sub>, PVP<sub>24</sub>, P4VPy, and P2VPy for the three NAIA-*co*-S members of the series, i.e., copolymers containing ethyl, propyl, and butyl chains in the itaconamic moiety. For those copolymers containing hexyl to dodecyl alkyl chains, phase separation is observed when the homopolymer is P2VPy. This result is attributed to highly steric hindrance because of the length of the side chain of the copolymer and to the location of the —N atom in position 2.

TABLE II  
Displacements of the Carbonyl and Aromatic Bands of the Homopolymers in the FTIR Spectra  
for Blends of NAIA-co-St 50% St with PVP10, PVP24, P2VPy, and P4VPy

Blend composition (w/w %)	$\Delta h$ (cm <sup>-1</sup> )			
	Carbonyl group PVP <sub>10</sub> /1655 cm <sup>-1</sup>	Carbonyl group PVP <sub>10</sub> /1655 cm <sup>-1</sup>	Aromatic group P2VPy/748 cm <sup>-1</sup>	Aromatic group P4VPy/820 cm <sup>-1</sup>
NEIA-co S 50% S				
80/20	6.8	7.5	3.5	6.0
60/40	7.8	7.3	2.0	6.2
50/50	7.6	7.8	1.8	7.0
40/60	5.6	5.9	1.0	6.8
20/80	11.4	9.7	0.9	7.2
NPIA-co-S 50% S				
80/20	5.2	7.8	2.0	3.8
60/40	5.0	8.3	2.2	4.2
50/50	6.5	5.8	1.8	3.3
40/60	4.0	6.0	2.2	3.2
20/80	5.1	7.0	2.3	3.5
NBIA-co-S 50% S				
80/20	4.8	5.0	1.0	4.2
60/40	5.0	3.5	2.8	3.7
50/50	4.7	3.8	2.0	3.9
40/60	4.3	3.6	1.8	4.6
20/80	4.0	3.3	2.2	4.5
NHIA-co-S 50% S				
80/20	3.7	3.0	1.1	4.0
60/40	3.5	2.9	0.8	3.8
50/50	3.6	2.9	1.0	3.9
40/60	3.3	3.0	0.8	3.7
20/80	3.3	3.1	0.8	3.3
NOIA-co-S 50% S				
80/20	3.5	2.9	1.1	3.5
60/40	3.6	3.0	1.1	3.4
50/50	3.4	2.8	1.0	3.5
40/60	3.2	2.3	0.7	3.6
20/80	3.0	2.5	0.8	3.0
NDIA-co-S 50% S				
80/20	2.8	2.0	1.3	2.8
60/40	2.8	1.9	1.0	2.9
50/50	2.4	2.1	1.1	2.9
40/60	2.5	2.2	0.6	2.4
20/80	2.4	1.7	0.7	2.4
NDoIA-co-S 50% S				
80/20	3.2	3.0	1.5	3.2
60/40	3.5	3.2	1.2	3.3
50/50	3.5	3.0	1.8	3.0
40/60	3.4	3.1	1.7	3.2
20/80	3.8	3.4	1.9	3.0

When the composition of alkyl itaconamic acid is increased, i.e., the copolymers have 50% of S, the behavior is rather different in the sense that one phase material is observed irrespective of the copolymer and the homopolymers involved. These results are confirmed by the DSC thermograms, by the GT and Cou values of the constants, and by the displacements in the FTIR spectra.

## References

- Lu, X., Weiss, R. A. *Macromolecules* 1991, 24, 4381.
- Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: Orlando, FL, 1978.
- Brus, J.; Dybal, J.; Schmidt, P.; Kratochvil, J.; Baldrian, J. *Macromolecules* 2000, 33, 6448.
- Ng, C. W. A.; MacNight, W. *Macromolecules* 1996, 29, 2412.
- Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1991, 29, 413.
- Paul, D. R.; Barlow, J. W.; Keskkula, H. *Mark-Bikales-Overberger-Menges: Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley: New York, 1988; Vol. 12, p 399.
- Cowie, J. M. G.; Guangxian, Li.; Ferguson, R.; McEwen, I. J. *J Polym Sci Part B: Polym Phys* 1992, 30, 1351.
- Brannock, G. R.; Paul, D. R. *Macromolecules* 1990, 23, 5240.
- Cowie, J. M. G.; Lath, D.; Makromol Chem Macromol Symp 1988, 16, 103.
- Shiomi, T.; Imai, K. *Polymer* 1991, 32, 73.
- Cowie, J. M. G.; Elexpuro, E. M.; McEwen, I. J. *J Polym Sci Part B: Polym Phys* 1991, 29, 407.

12. Kambour, R. P.; Bendler, J. T.; Boop, R. C. *Macromolecules* 1983, 16, 753.
13. Ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* 1983, 16, 1827.
14. Luo, X.; Goh, S. H.; Lee, S. Y. *Macromolecules* 1997, 30, 4934.
15. Urzúa, M.; Gargallo, L.; Radić, D. *J Macromol Sci Phys* 2000, 39, 143.
16. Urzúa, M.; Opazo, A.; Gargallo, L.; Radić, D. *Polym Bull* 1998, 40, 63.
17. Urzúa, M.; Gargallo, L.; Radić, D. *J Macromol Sci Pure Appl Chem* 2000, 37, 37.
18. Opazo, A.; Gargallo, L.; Radić, D. *Polym Bull* 1996, 36, 511.
19. Belorgey, G.; Prudhomme, R. *J Polym Sci Polym Phys Ed* 1982, 20, 91.
20. Radić, D.; Gargallo, L. *Thermochim Acta* 1991, 180, 241.
21. Paul, D. R.; Newman, S. *Polymer Blends*; Academic Press: New York, 1978.
22. Hubbel, D. S.; Cooper, S. L. *J Appl Polym Sci* 1977, 21, 3035.
23. Brode, G. L.; Koleske, J. V. *J Macromol Sci Chem* 1972, 6, 1109.
24. Ong, C. J.; Price, F. P. *J Polym Sci Polym Symp* 1969, 63, 59.
25. Koleske, J. V.; Lundberg, R. D. *J Polym Sci* 1969, 2, 765.