

Blends Containing Amphiphilic Polymers IV. Poly(N-1-alkyl Itaconamic Acids) with Poly(2-vinylpyridine) and Poly(4-vinylphenol)

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Received 19 April 2001; accepted 15 September 2001

ABSTRACT: The phase behavior of blends containing Poly(N-1-alkyl itaconamic acids) (PNAIA) with Poly(2-vinylpyridine) (P2VPy) and Poly(4-vinylphenol) (P4VPh) were analyzed by Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared Spectroscopy (FTIR). Miscibility over the whole range of compositions is observed in both systems. All the blends show thermograms exhibiting distinct single glass transition temperatures (T_g), which are intermediate to those of the pure components. The Calorimetric Analysis using Gordon Taylor, Couchman, and Kwei treatments allows conclusion that interactions between the components is favorable to the miscibility. FTIR analysis of the blends suggests that the driving force for miscibility is hydrogen bonding formation. The variation of the absorptions of the carbonyl groups of PNAIA and the hydroxyl groups of P4VPh allows one to attribute the miscibility to weak acid base like interactions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1245–1250, 2002; DOI 10.1002/app.10453

Key words: functionalization of polymers; polymer blends; amphiphiles; miscibility

INTRODUCTION

Miscibility in polymer blends results from the negative value of Gibbs free energy of mixing, ΔG_m . This term combines the effects of both entropy and enthalpy. Polymer–polymer miscibility is a process enthalpically governed because the entropic contribution is vanishingly small for high molecular weights. Therefore, to ensure a mixing process with only one-phase material, the heat of mixing, which reflects the contact interactions between dissimilar components, must be negative or at least not significantly positive. For

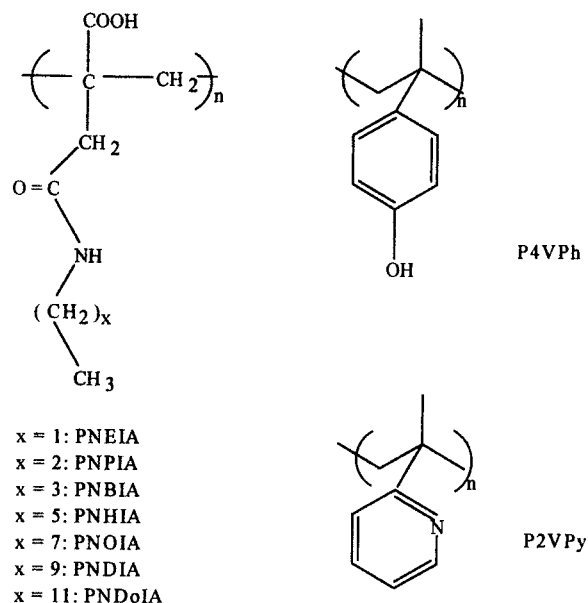
this reason in the mixing process it is necessary to ensure interactions between the components of the blend. This can be obtained through the combination of polymers with repeat units where specific interactions between the chains can exist, and the heat of mixing between components should be favorable. The functionalization by incorporation of interacting groups in the macromolecular chain is a way to reach this objective. Dipole–dipole, donor–acceptor or acid–base interactions could take place. Basic polymers such as Poly(vinylpyridine)s are miscible with proton-donating polymers such as Poly(4-vinylphenol) (P4VPh),^{1,2} Poly(acrylic acid) (PAA),^{3,4} and Poly(monoalkyl itaconates) (PMAI)⁵ due to hydrogen bonding formation. Poly(4-vinylpyridine) (P4VPy) is miscible with several polymers containing acidic groups.^{1–8} Hydrogen bond formation has been considered as critical to enhancing the miscibility in these systems.

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Contract grant sponsor: FONDECYT; contract grant numbers: 1010726, 2970009, and 4880028.

Contract grant sponsor: DIPUC.

Journal of Applied Polymer Science, Vol. 84, 1245–1250 (2002)
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Scheme 1

Poly(N-1-alkylitaconamic acids) (PNAIA) are a family of functionalized polymers derived from itaconic acid, containing a free carboxylic group and an amide group per repeating unit (see Scheme 1). These polymers can be multifunctionalized and also modified by inserting long side chains with different lengths, as side groups thus resulting in polymers with different hydrophobicity.^{9–11} This structural characteristic is very useful when these polymers are used in different systems such as polymer blends.^{11,12} Due to this interacting structure, PNAIA are interesting in the compatibilization process with weak basic and acidic polymers because it can interact by acid–base interaction through the free carboxylic group and or the amidic carbonyl group.

The aim of the present work is the study of the compatibilization process of Poly(N-1-alkyl itaconamic acids) containing ethyl (PNEIA), propyl (PNPIA), butyl (PNBIA), hexyl (PNHIA), octyl (PNOIA), decyl (PNDIA), and dodecyl (PNDolA) groups with weak basic and weak acidic polymers, i.e., Poly(2-vinylpyridine) (P2VPy) and Poly(4-vinylphenol) (P4VPh) (Scheme 1). This way it should be possible obtain confidence about the strength of the interaction of PNAIA with these weak acid and basic polymers.

EXPERIMENTAL

Monomers and Polymers Preparation

N-1-alkylitaconamic acids (NAIA) were synthesized by reaction of itaconic anhydride with the

corresponding 1-alkylamine in chloroform, following procedures previously reported and improved by us.^{10–13} Polymers, PNEIA, PNPIA, PNBIA, PNHIA, PNOIA, PNDIA, and PNDolA were obtained by radical polymerization in bulk at 343–393 K (depending on the N-1-alkylitaconamic acid used) under nitrogen, using α, α' -azobisisobutyronitrile (AIBN) (0.6% mol) as initiator. Purification of the polymers was achieved by reprecipitation with methanol in THF solution, before vacuum drying. Poly(2-vinylpyridine) and Poly(4-vinylphenol) both with weight average molecular weight $\bar{M}_w = 20,000$ were commercial samples from Aldrich.

Preparation of the Blends

Blends of different compositions were prepared by solution casting using chloroform as the solvent for those containing P2VPy, and THF for those of P4VPh, 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 DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Dry nitrogen was used as purge gas, and thermograms were measured in the range 308 to 523 K at a scan rate of 20° min⁻¹.

FTIR Measurements

Infrared spectra of pure polymers and blends were recorded on a Vector 22 Bruker Fourier Transform Infrared spectrophotometer. The spectra were recorded with a resolution of 1 cm⁻¹. The samples were prepared directly in KBr pellets.

RESULTS AND DISCUSSION

Dry blends of PNAIA with P2VPy and P4VPh were transparent, and showed thermograms exhibiting distinct single glass transition temperatures (T_g). Figure 1 shows the variation of T_g with the composition for blends of PNAIA with P2VPy and P4VPh with seven different Poly(N-1-alkylitaconamic acids) (PNAIA), i.e., Poly(N-1-ethyl, propyl, butyl, hexyl, octyl, decyl and dodecyl itac-

onamic acid); (PNEIA), (PNPIA), (PNBIA), (PNHIA), (PNOIA), (PNDIA), and (PNDoIA), respectively. A continuous variation of T_g , where values are intermediate between the T_g of the pure components is observed. This behavior would indicate miscibility over the whole range of composition, irrespective of the PNAI considered in the blends and if the blend contains P2VPy or P4VPh. However, there are differences in the shape of the curves, and the degree of curvature is low and rather different for the systems analyzed. Blends containing P2VPy show curves with no important differences in the weighed values of T_g between the pure components and almost no curvature is observed. In the case of blends with P4VPh, curves over the weighed values of T_g between the pure components with the exception of the blend

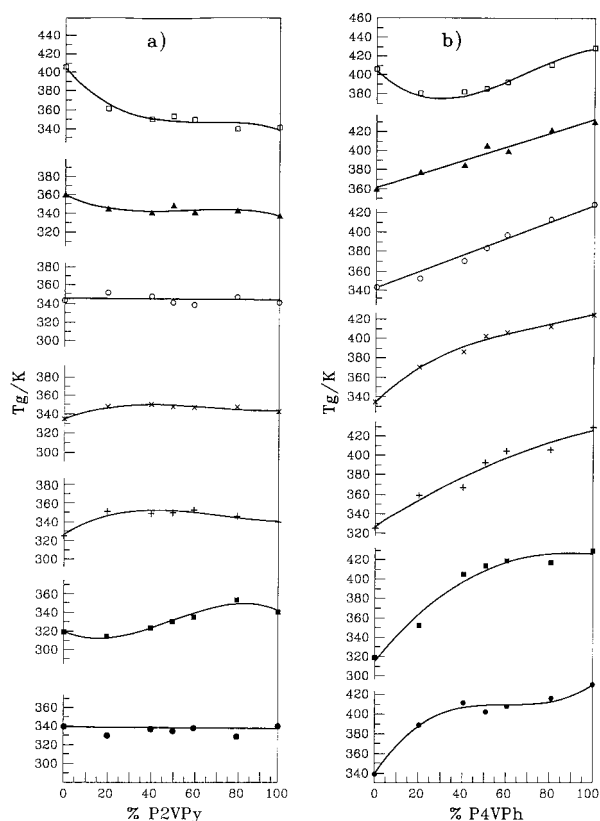


Figure 1 Variation of the glass transition temperature (T_g) for blends of (a) Poly(N-1-alkyl itaconamic acids (PNAIA) with Poly(2-vinylpyridine) (P2VPy). (\square) PNEIA/P2VPy; (\blacktriangle) PNPIA/P2VPy; (\circ) PNBIA/P2VPy; (\times) PNHIA/P2VPy; (+) PNOIA/P2VPy; (\blacksquare) PNDIA/P2VPy; (\bullet) PNDoIA/P2VPy, and (b) PNAIA with Poly(4-vinylphenol) (P4VPh). (\square) PNEIA/P4VPh; (\blacktriangle) PNPIA/P4VPh; (\circ) PNBIA/P4VPh; (\times) PNHIA/P4VPh; (+) PNOIA/P4VPh; (\blacksquare) PNDIA/P4VPh; (\bullet) PNDoIA/P4VPh.

Table I Gordon Taylor (K_{GT}) and Couchman (K_{Cou}) Constants for Blends of PNAIA with P2VPy and P4VPh

Polymer	P2VPy		P4VPh	
	K_{GT}	K_{Cou}	K_{GT}	K_{Cou}
PNEIA	0.77	0.63	0.45	0.47
PNPIA	0.49	0.51	0.46	0.45
PNBIA	0.44	0.47	0.62	0.63
PNHIA	0.19	0.21		

containing PNEIA/P4VPh can be observed [top of Fig. 1(b)]. The curvature of the plots are not quite different from those of the blend containing P2VPy [Fig. 1(a)]. To analyze in a quantitative way the variation of T_g with the blend composition for these systems, the Gordon Taylor¹⁴ (GT) and Couchman¹⁵ (Cou) treatment of the data were used. From this procedure it is possible to estimate the strength of the interaction. Table I summarizes the Gordon Taylor and Couchman constants K_{GT} and K_{Cou} for all the systems studied.

These parameters have been considered as a semiquantitative measure of the strength of the interaction between the interacting groups of the polymeric components.¹⁶ The K_{GT} and K_{Cou} values compiled in Table I would indicate that the interaction between the polymeric components is enough to favor polymer-polymer miscibility. However, the above procedures are not the best fitting methods because they cannot describe S-shaped curves. These curves are commonly fitted by the Kwei¹⁷ equation:

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

where w_i represents the weight fractions of the components, T_g the glass transition temperature of the blend, and T_{gi} the glass transition corresponding to the pure components. For the case of S-shaped curves exhibited in Figure 1 they can be represented satisfactorily by the equation:

$$T_g = \frac{(w_1 T_{g1} + k w_2 T_{g2})}{(w_1 + k w_2)} + q w_1 w_2 \quad (2)$$

Equation (1) is clearly a special case of eq. (2) when $k = 1$. Figure 2 shows the fitting of T_g for three different blends as an example of the general behavior. Table II summarizes k and q values

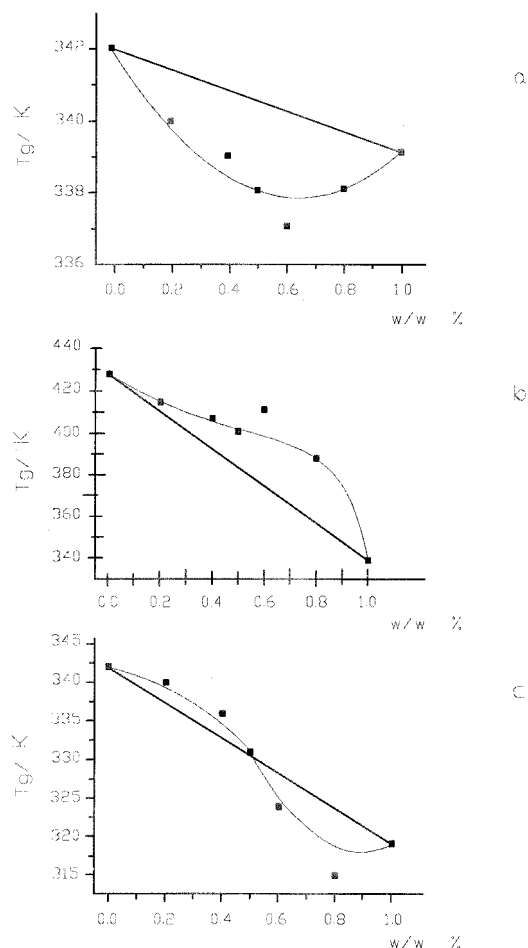


Figure 2 Glass transition temperature of blends of (a) PNDIA/P4VPh, (b) PNDIA/P4VPh, (c) PNDIA/P4VPh according to the Kwei fitting of the curve.

for the fitting of all the blends studied here. The correlation coefficient for the best fit in each case is also summarized in this Table II. The values of k and q obtained by this procedure are in good

Table II Kwei Constants for Blends of PNAIA with P2VPy and P4VPh

Polymer	PNAIA/P2VPy			PNAIA/P4VPh		
	k	q	r	k	q	R
PNEIA	0.2	1.0	0.97	0.5	5.0	0.96
PNPIA	0.2	2.0	0.98	0.7	9.0	0.95
PNBIA	2.0	3.0	0.97	0.8	14.0	0.98
PNHIA	4.0	21.0	0.98	4.0	30.0	0.91
PNOIA	5.0	25.0	0.97	2.0	47.0	0.88
PNDIA	12.0	82.0	0.96	2.0	96.0	0.95
PNDIA	10.0	10.0	0.97	7.0	63.0	0.99

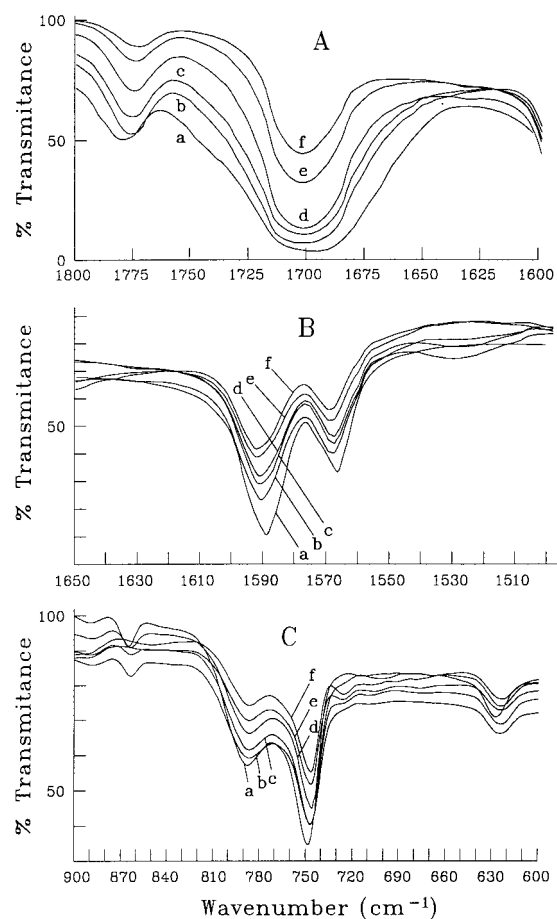


Figure 3 FTIR spectra for blends of PNHIA with P2VPy. (A) Vibration of carboxyl and amide carbonyl groups of PNHIA. (B) Stretching pyridine aromatic ring region. (C) Bending pyridine aromatic ring region. (a) PNHIA, (b) PNHIA/P2VPy 80/20 (w/w), (c) PNHIA/P2VPy 60/40 (w/w), (d) PNHIA/P2VPy 50/50 (w/w), (e) PNHIA/P2VPy 40/20 (w/w), and (f) PNHIA/P2VPy 20/80 (w/w).

agreement with those reported for other systems. By this way it is possible to assume that there is an important interaction between the components of the blends, which is responsible to the compatibility. On the other hand, annealed blends show one single enthalpy relaxation peak which is indicative of miscibility.

To obtain further information about the interactions involved, FTIR measurements were performed. Intra- and intermolecular association in PNAIA cannot be disregarded because of the carboxylic and amide groups. Figure 3 shows the infrared spectra of blends of PNHIA/P2VPy as an example of the general behavior of this kind of blends. Figure 3(A) shows the FTIR spectra in the

region of the carbonyl valence vibrations from 1600 to 1800 cm^{-1} . This region corresponds to the vibration of the carbonyls of the free carboxylic and amide groups respectively at different blend compositions. The band at 1700 cm^{-1} corresponding to the vibration of the carbonyl of the amide group remains unchanged, and no shift relative to the pure PNHIA is observed. However, the vibration band at 1780 cm^{-1} of the carbonyl of the free carboxylic group is shifted to 1767 cm^{-1} as the amount P2VPy increases in the blend. This result would be indicative of interaction between the carboxylic group of PNHIA with P2VPy. In agreement with this result the bands of the aromatic ring of pyridine groups shown in Figure 3(B) and (C) are shifted from 1593 to 1588 cm^{-1} and from 748 to 745 cm^{-1} , respectively. This spectroscopical behavior is indicative of the fact that interactions like hydrogen bonding are present in such binary systems. It is possible to assume that the free carboxylic group of PNAIA is able to interact with the pyridine ring of P2VPy. The interaction between PNAIA and P2VPy could be like weak acid–base interaction due to the hydrogen bond interaction between the carboxylic —OH and pyridinic nitrogen. This weak interaction should be sufficient to favor compatibility between the polymers under study.

Figure 4(A) shows the typical FTIR spectra of blends containing PNAIA and P4VPh in the hydroxyl valence vibration region. In this case we have considered the blend PNBIA/P4VPh as a representative example of the general behavior of the blends. For pure P4VPh the —OH vibration is separated into two distinct bands.^{1,18} The first, corresponding to a broad distribution of self-associated hydroxyl groups,^{1,18} is centered about 3330 cm^{-1} . The second contribution assigned to free hydroxyl groups is centered about 3530 cm^{-1} . In the case of blends with PNAIA the —NH band of the amido group is overlapped with the OH band. Nevertheless, in the blends of PNAIA with P4VPh only one band can be detected, indicating that within experimental error all hydroxyl groups of P4VPh form hydrogen bonds inter or intraassociated. In fact, as the PNAIA content in the blend increases the intensity of the free hydroxyl band at 3530 cm^{-1} decreases and almost disappears, indicating that at least free hydroxyl groups are involved in intermolecular association with PNAIA. Meanwhile, the peak is shifted where it is indicative of strong hydrogen bonding between PNAIA and P4VPh. On the other hand, in the region of 1600–1800 cm^{-1} , where the absorption

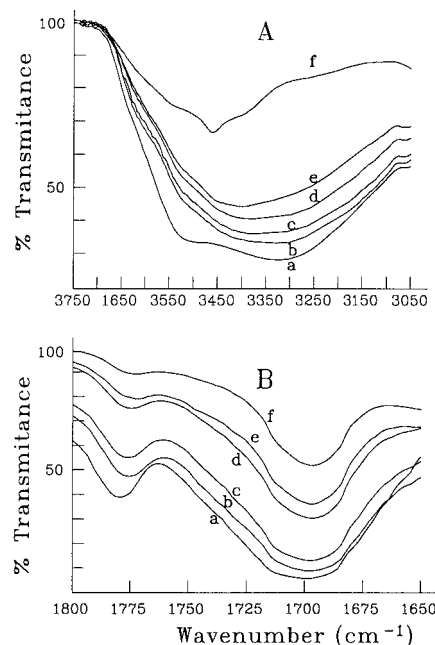


Figure 4 FTIR for blends of PNBIA with P4VPh. (A) Hydroxyl valence vibration region. (B) Vibration of carbonyl and amide carbonyl groups of PNBIA (a) P4VPh, (b) PNBIA/P4VPh 20/80 (w/w), (c) PNBIA/P4VPh 40/60 (w/w), PNBIA/P4VPh 50/50 (w/w), PNBIA/P4VPh 60/40 (w/w), PNBIA/P4VPh 80/20 (w/w).

of the carboxylic and amide carbonyl groups appears, it is possible to observe an important shift of the band corresponding to the carboxylic group at 1780 cm^{-1} as the PNAIA content increases [Fig. 4(B)]. However, the band corresponding to amide carbonyl group remains unchanged. Therefore, these results would indicate that the interaction between the components of the blend takes place through hydrogen bonding formation between the acidic carbonyl group of PNAIA and the P4VPh hydroxyl group. In this case as in the former, the miscibility can be attributed to a weak acid–base interaction via hydrogen bonding formation.

CONCLUSIONS

Both DSC and FTIR were used to investigate the phase behavior of blends containing PNAIA with P2VPy and P4VPh. Miscibility over the whole range of composition is found. In both systems weak hydrogen bonding interaction between the components is observed and, therefore, a weak

acid–base interaction can be considered as the driving force for miscibility.

We express our thanks to FONDECYT, Project 1010726, for partial financial support. M.U thanks to FONDECYT projects 2970009 and 4880028. The financial help from DIPUC is also acknowledged.

REFERENCES

1. Luo, X.; Goh, S. H.; Lee, S. Y. *Macromolecules* 1997, 30, 4934.
2. Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polym J* 1994, 36, 906.
3. Fujimori, K.; Costigan, M. J.; Trainor, G. T. *J Polym Sci Polym Chem Ed* 1984, 22, 2479.
4. Oyama, H. T.; Nakajima, T. *J Polym Sci Polym Chem Ed* 1983, 21, 2987.
5. Gargallo, L.; Gatica, N.; Radić, D. *Int J Polym Mater* 1994, 27, 107.
6. de Ilarduya, A. M.; Eguburi, J. L.; Espi, E.; Iruiñ, J. J.; Fernández-Berridi, M. J. *Makromol Chem* 1993, 194, 501.
7. Gargallo, L.; Gatica, N.; Radić, D. *Int J Polym Mater* 1994, 27, 107.
8. Velada, E.; Cesteros, L. C.; Katime, I. *Appl Spectrosc* 1996, 50, 893.
9. Oishi, T. *Polym J* 1980, 12, 719.
10. Urzúa, M.; Opazo, A.; Gargallo, L. Radić, D. *Polym Bull* 1998, 40, 63.
11. Urzúa, M.; Gargallo, L. Radić, D. *J Macromol Sci Pure Appl Chem* 2000, A37, 37.
12. Urzúa, M.; Gargallo, L. Radić, D. *J Macromol Sci Phys* 2000, B39, 143.
13. Opazo, A.; Gargallo, L.; Radić, D. *Polym Bull* 1996, 36, 511.
14. Gordon, M.; Taylor, J. *J Appl Chem* 1952, 2, 493.
15. Couchman, P. R. *Polym Eng Sci* 1984, 24, 135.
16. Belorgey, G.; Prud'Homme, R. *J Polym Sci Polym Phys* 1982, 20, 191.
17. Kwei, T. K. *J Polym Sci Polym Lett* 1984, 22, 307.
15. Li, D.; Brisson, J. *Macromolecules* 1996, 29, 868.