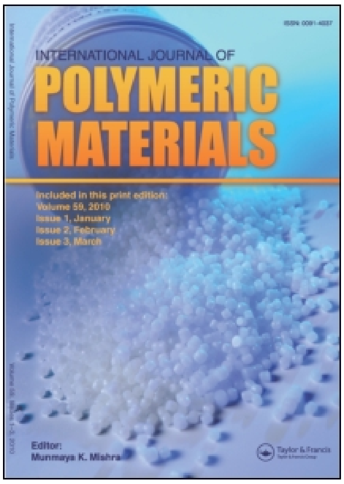

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Blends of Poly(monoalkylitaconates)/ Poly(vinylpyridines) and Model Molecules

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The compatibility in blends containing poly(monoalkylitaconates) (PMAI) and poly(vinylpyridines (PVPy) by several analytic techniques i.e. viscometry, UV-VIS spectrophotometry, Differential Scanning Calorimetry (DSC) Furier Transform Infrared Spectrophotometry (FTIR) was studied. Blends of PVPy with PMAI give rise to insoluble products irrespective of the starting composition, which can be attributed to interpolymer complex formation. From UV-VIS it is possible to observe miscibility behaviour between polymers. By DSC the thermograms observed are similar to those of PMAI but different from those of pure PVPy. A variation of the wavenumber of the carbonyl group of PMAI with composition is observed by FTIR, which is another argument to suspect miscibility. In order to study the effect of the molecular weight of the components on the miscibility, the analysis of blends containing PVPy and the corresponding poly(moalkylitaconates) monomer analogues was performed. Compatibility is observed in these cases but with important differences between the magnitudes of the variations relative to the polymeric blends. Miscibility is unfavoured as the molecular weight of the components increases, in good agreement with theory.

KEY WORDS Blends, poly(monoalkylitaconates), poly(vinylpyridines), succinic acid derivatives, miscibility, compatibility.

INTRODUCTION

Miscibility in polymer blends is a matter of current interest both from academic and industrial point of view. It is well known that miscibility in polymer blends most often is the result of favourable, exothermic interactions between the blend components which is possible to promote, selecting dissimilar structures.[1,5] In order to ensure miscibility it is necessary to match polymer repeat units carefully or to ensure that some favourable specific interactions can exist between the chains.[4] This can be achieved through dipole-dipole or donor-acceptor interactions by incorporating acid and base functions.[5] In these systems strong interactions take place and when such specific interactions occur at frequent intervals along the chain (in the limit at every repeat unit) a so-called polymer-polymer complex with very well defined stoichiometry may result.[4,5,6] Poly(monoitaconates) are a family of vinyl

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polymers which have a free carboxyl group and therefore can interact by hydrogen bonding with acceptor polymers giving rise to interpolymer complexes.[7,8] These polymer complexes have been broadly studied due to the interest in preparing compatible polymer blends.[9-12] Nevertheless one of the most important factors to take into account in such systems is the nature of the interactions involved in the blend and the effect of the polymer structure on the miscibility or in the complex formation.

The aim of the present work is the study of the compatibility of polymeric blends in order to identify the effect of specific interactions on the miscibility and to compare these interactions using blend components of different molecular weights. In order to reach this objective, blends of poly(2-vinylpyridine) (P2VPy) and poly(4-vinylpyridine) (P4VPy) with poly(monoMethylitaconate) (PMMI) and poly(monoethylitaconate) (PMEI) were studied by viscometry, UV-VIS spectrophotometry, Furier Transform Infrared Spectrophotometry (FTIR) and Differential Scanning calorimetry (DSC). Blends containing the corresponding monoitaconates monomeric analogues i.e. succinic acid and derivatives, were also analyzed by the same experimental techniques in order to compare the interactions involved with model small molecules.

EXPERIMENTAL

Model Molecules

Commercial samples of succinic acid (SA), methylsuccinic acid (MSA) and methyl succinate (MS) from Aldrich were used.

Monomers and Polymers Preparation

Poly(vinylpyridines). Commercial samples of poly(2-vinylpyridine) (P2VPy) and poly(4-vinylpyridine) (P4VPy) from Polyscience were used.

Poly(monoitaconates). Monomethylitaconate and monoethylitaconate were obtained by esterification of itaconic acid with the corresponding alcohols according to the techniques previously reported.[13-15] Poly(monomethylitaconate) (PMMI) and poly(monoethylitaconate) (PMEI) were obtained by radical polymerization as previously reported.[13-15]

Preparation of the blends. Blends of different compositions were prepared by solution casting from methanol and then evaporated at room temperature and vacuum dried at 298°K for 72 h. The polymer concentration in the solution was about 2% (w/w).

DSC Measurements

The glass transition temperatures (Tg) of the different polymers and blends were measured with a Mettler TA-3000 system equipped with a TC-A 10 Processor with a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior to the measurements. Samples were weighed into the DSC aluminum pans. Dry nitrogen were used as purge gas and thermograms were measured in the range 308 K to 393 K, at a scan rate of 10 K/min. Regular calibration of the instrument was carried using pure metal standards. Samples were annealed at the upper limit temperature and then quenched to the lower limit temperature in order to minimize the thermal history.

UV-VIS Measurements

UV-VIS absorption spectra of the pure products and blends of PMAI and PVPy and small model molecules with PVPy were recorded in UV-VIS Perkin-Elmer Lambda 3-B spectrophotometer using methanol as common solvent at 298 K. Blends were prepared covering the whole composition range of poly(acids) as well as model molecules and the corresponding poly(bases). Highly diluted solutions were employed because of absorbance reasons and to avoid coprecipitation of the components. The concentrations used were 0.06 gL^{-1} for model molecules and 0.08 gL^{-1} for blends of PVPy and PMAI.

Viscometry Measurements

Intrinsic viscosity $[\eta]$ of the different blends were determined using a Desreux-Bischoff[16] capillary dilution viscometer in methanol at 298 K without kinetic energy corrections. Intrinsic viscosities were obtained by extrapolation of the classical Huggins equation.[17]

FTIR Measurements

FTIR measurements were performed in a Bruker IFS-25 spectrophotometer in KBr. Spectra were obtained with a resolution of 2 cm^{-1} and 64 scans were accumulated. Spectra were analyzed through the computer system of the instrument.

RESULTS AND DISCUSSION

P2VPy and P4VPy show a very clear Tg value at 327 and 343 K respectively but in the case of PMAI the Tg value is very difficult to detect as has been reported.[5,18,19] In blends of P2VPy and P4VPy with PMAI, the Tg value of the blend or the Tg value corresponding to the pure components cannot be detected. This is a very interesting result because it is difficult to attribute this behaviour to miscibility between the components, but if phase separation takes place, the Tg value corresponding to the pure polymers should be clearly detected. Therefore, in the systems here described, it is possible to suspect that some kind of interaction should be present between PMAI and PVPy. This could be an acid-base interaction (association), giving rise to a polysalt. On the other hand, when solutions of the blends in methanol, which is a good common solvent for both type of polymers, are prepared, co-precipitation takes place irrespective of the initial composition and insoluble products are formed. This result could be attributed to interpolymer complex formation between PMAI and PVPy by donor-acceptor interaction, what seems to be a reasonable result taking into account the polymer structures. In fact, it seems reasonable to think that mixing a poly(acid) with a poly(base), association is promoted giving rise to a diminishing of the solubility of the polymeric complex in water and/or polar solvents, due to the tendency of polymeric particles to form globules.[5] Intrinsic viscosity measurements could be an interesting way in order to analyze miscibility between polymers, because viscometry detects the totality of mixed species at molecular level and is independent of the morphological state of the polymers. Besides, it is possible to detect phase inversions if they occur. However, in blends of PMAI with PVPy it was impossible to make these determinations due to the insolubility of the formed product.

Very dilute solutions of the pure polymers and blends are soluble and the UV-VIS spectra can be registered. Poly(vinylpyridines) show a maximum in absorbance at $\lambda_{max} = 206$ nm and when are blended with PMAI there is an increasing of λ_{max} to 210 nm. This value remains approximately constant as the composition increases while blend is present in the solution and then falls down to the value of $\lambda_{max} = 202$ nm corresponding to pure PMAI. The same behaviour is observed using both P2VPy and P4VPy with PMAI. This behaviour could be interpreted as an evidence of interaction of the type donor-acceptor giving rise to an adduct between components of the blend and also as evidence of compatibility. Because of the insolubility, which could be due not only to interpolymer complex formation but to the effect of the molecular weight, blends of PVPy with poly(itaconates) analogues small molecules were prepared in order to clarify the interactions involved in these systems.

Blends of PVPy with succinic acid and derivatives such as methylsuccinic acid and methylsuccinate were studied by UV-VIS. Figure 1 shows the variation of λ_{max} of PVPy with composition. It is noteworthy that λ_{max} increases sharply for low composition blends containing succinic acid derivatives and then decreases monotonously with composition. Clearly in this case the displacement should be attributed to an acid-base type association between PVPy and succinic acid derivatives. This behaviour is similar to that found for blends containing polymers, but in the case of small molecules the magnitude of the effect is larger. Therefore, in the case of blends in which both components are macromolecules, it seems reasonable to assume that the acid-base type association is less strong due to steric hindrance, which is absent in small molecules.

Intrinsic viscosity $[\eta]$ of blends of PVPy with succinic acid derivatives were measured in methanol at 298 K. Figure 2 shows the variation of $[\eta]$ with composition for different mixtures. A monotonous diminishing of $[\eta]$ with composition is observed. This is an expected result because as the content of the small molecules increases the polymeric content also diminishes. The decrease of intrinsic viscosity could be also attributed to a compaction of the polymeric molecules due to the neutralization by the acid as is the case of blends between poly(acids) and poly(bases) in solution and in the solid state as was previously reported.[5,7-9] On the other hand DSC thermograms of these blends in general show an important decrease in Tg values of PVPy with small amounts of the model molecules. These results are in good agreement with those reported by UV-VIS and viscometry.

FTIR measurements are a powerful tool in order to analyze compatibility in polymer blends. Films of PVPy with PMAI were prepared and the FTIR spectra

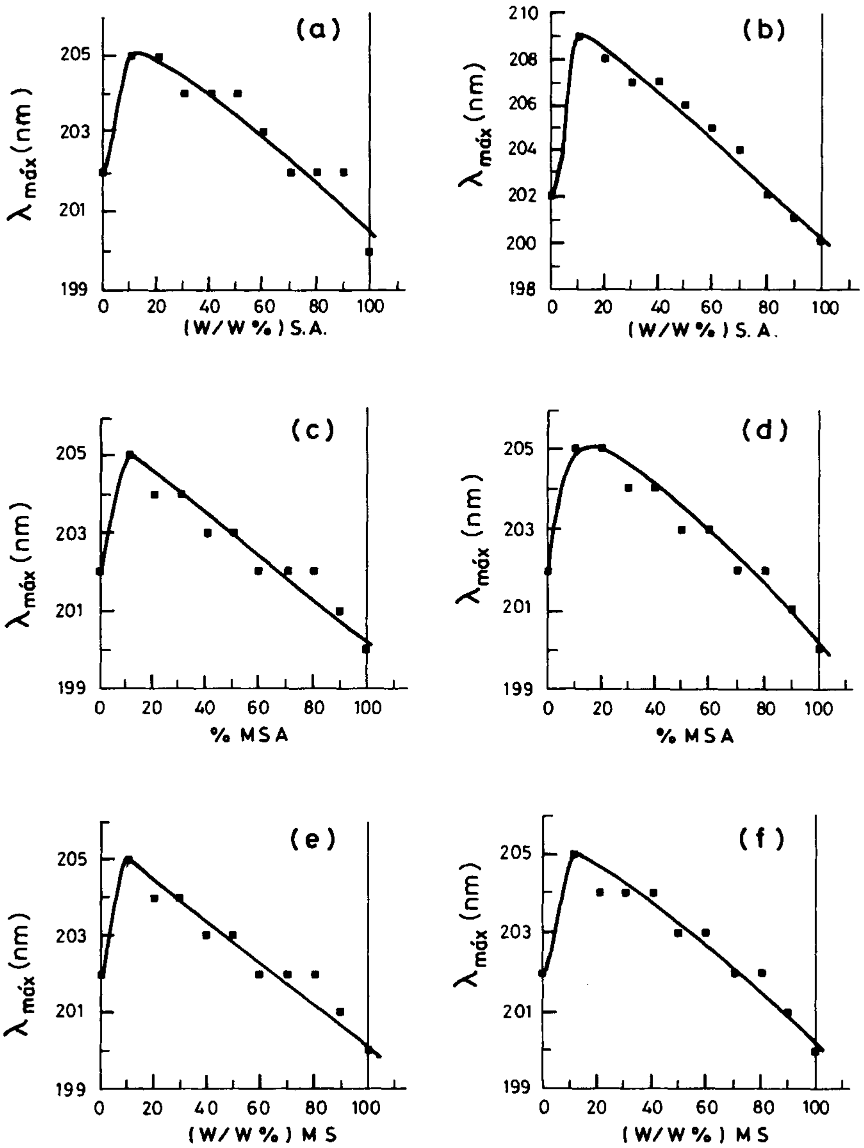

FIGURE 1 Variation of $\lambda_{máx}$ with composition in methanol at 298 K a) P2VP-SA; b) P4VPy-SA; c) P2VPy-MSA; d) P4VPy-MSA; e) P2VPy-MS; f) P4VPy-MS.

were recorded. A shift of the band at 1730–1740 cm^{-1} corresponding to the bending vibration of the carbonyl of PMAI is observed. This shift could be attributed to an interaction of the hydrogen bonding type between the carboxyl group of PMAI with the basic group of PVPy. In all cases a displacement of the wavenumber of the C=O group is detected when small amounts of PVPy are added and this displacement increases with composition except in blends of P2VPy-PMAI where the shift remains practically constant. This result could be due to the differences

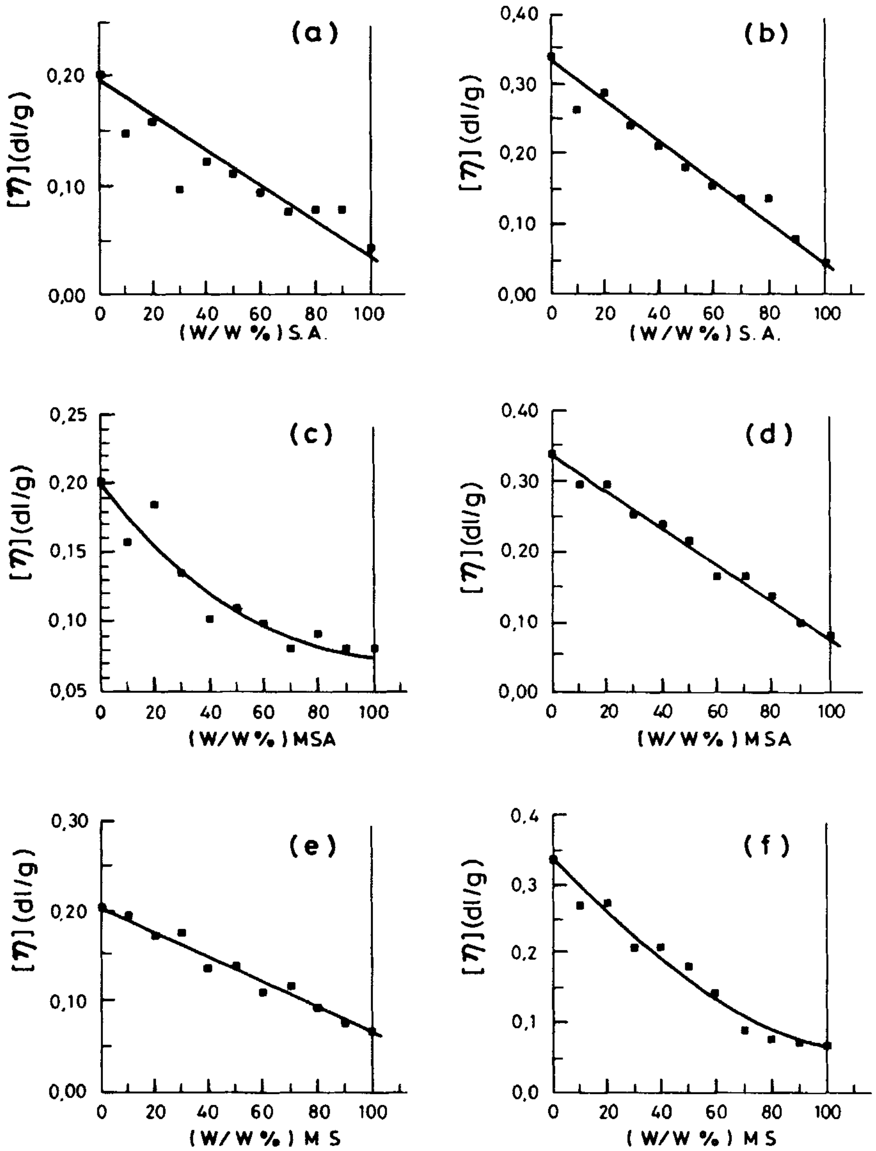

FIGURE 2 Variation of [η] with composition in methanol at 298 K. a) P2VP-SA; b) P4VPy-SA; c) P2VPy-MSA; d) P4VPy-MSA; e) P2VPy-MS; f) P4VPy-MS.

in the interactions involved when the PVPy nitrogen is located in position 2 or 4. In the former, the steric hindrance is larger and therefore the magnitude of the interaction is minor. It can be observed that in blends containing polymers as well as in those containing monomeric analogues a variation in the wavenumber of the carbonyl group of PMAI is always present. However, the variations are more pronounced in mixtures with small molecules. It is also noteworthy to observe the

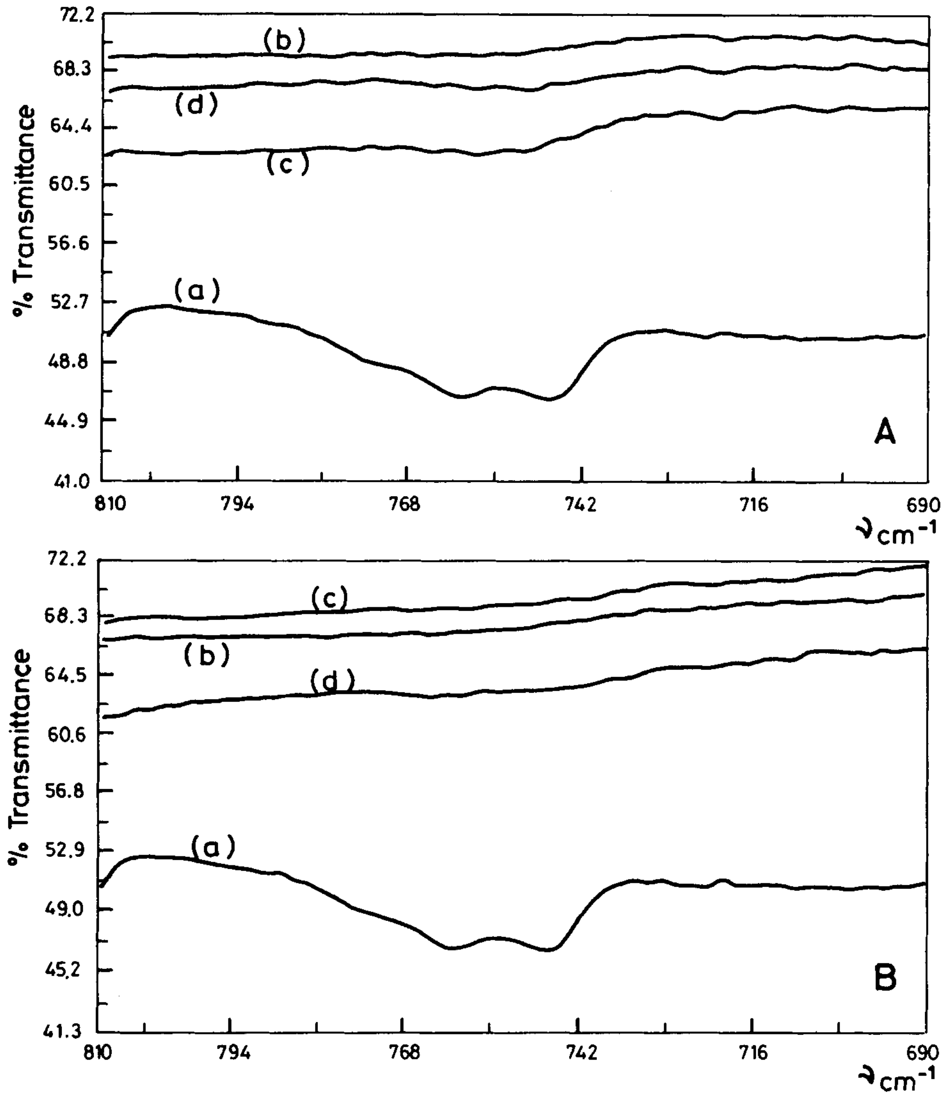

FIGURE 3 FTIR spectra in the zone of aromatic substitution 810-690 cm^{-1} for different blends at four compositions. A) Blends of P4VPy-PMMI: a) P4VPy; b) P4VPy 90%; c) P4VPy 50%; d) P4VPy 10%. B) Blends of P4VPy-PMEI: a) P4VPy; b) P4VPy 90%; c) P4VPy 50%; d) P4VPy 10%.

zone of the spectrum corresponding to the substitution of the aromatic ring. Figures 3 and 4 show this zone of the spectrum for different blends of PVPy and PMAI. The differences observed in the spectra could be due to differences in the nature of the interactions. For blends of P4VPy-PMMI and P4VPy-PMEI it is possible to observe the absence of the band corresponding to the aromatic substitution as can be seen in Figure 3-A and 3-B. This band disappears irrespective of the composition analyzed. For P2VPy-PMMI and P2VPy-PMEI blends (see Figure 4-A and 4-B) the band corresponding to substitution is always present irrespective of the com-

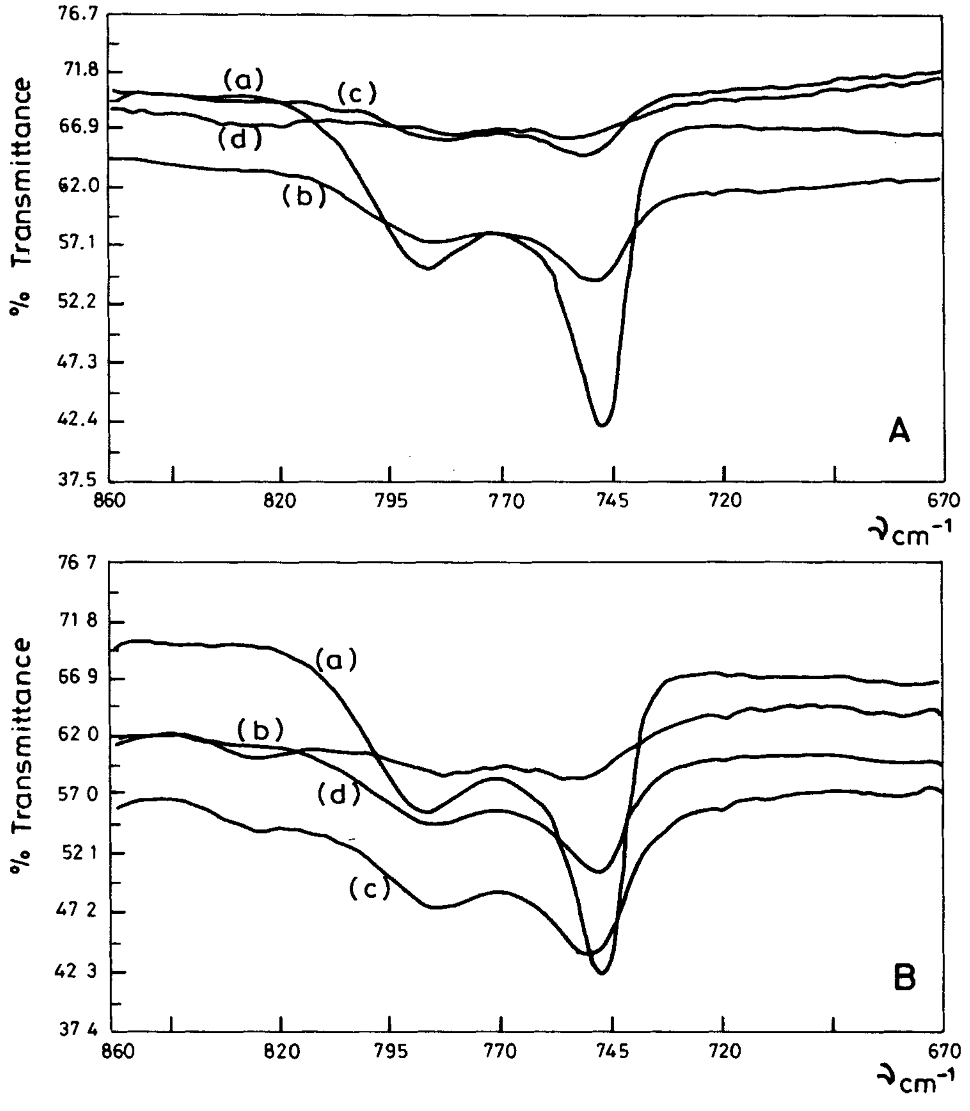

FIGURE 4 FTIR spectra in the zone of aromatic substitution 860-670 cm^{-1} for different blends at four compositions. A) Blends of P2VPy-PMMI: a) P2VPy; b) P2VPy 90%; c) P2VPy 50%; d) P2VPy 10%. B) Blends of P2VPy-PMEI: a) P2VPy; b) P2VPy 90%; c) P2VPy 50%; d) P2VPy 10%.

position of the blend. This result should be a consequence of the interactions between basic and acid groups of P4VPy with PMMI and PMEI where the interaction would modify in some way the pyridinic aromatic system. The fact that only in blends containing P4VPy the band corresponding to the aromatic substitution disappears is explained in terms of the better accessibility of the basic group in P4VPy from steric hindrance point of view. Similar results are observed when blends are prepared with small analogues molecules, what is another argument to consider miscibility by acid-base association in these systems.

CONCLUSIONS

A general miscibility should be assumed in blends of PVPy and PMAI and the corresponding monomeric analogues. According to the results here reported the miscibility in these systems is explained due to donor-acceptor interactions with formation of interpolymer complex with a polysalt structure. The steric hindrance due to the macromolecular structure seems to be an important factor to take into account in order to promote miscibility in these polymer blends. In fact the general behaviour of blends containing P2VPy or P4VPy is rather different and the differences are attributed only because of the position of the basic group in the pyridine ring.

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