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Polymer–polymer complexation between poly(monomethyl itaconate) and poly(vinylpyridine)s

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Polymer–polymer hydrogen-bonded complexes of poly(monomethyl itaconate) with poly(2-vinylpyridine) and poly(4-vinylpyridine) were studied. Several solvents have been assayed for these systems: methanol, methylformamide and binary mixtures (50/50) of methanol with water, tetrahydrofuran, dimethylformamide and dimethylacetamide. In all cases, instantaneous precipitate formation was observed after mixing the solutions of poly(monomethyl itaconate) and poly(vinylpyridine)s. Polymer complexes prepared from methanol solutions show different stoichiometries depending on the feed composition, but that found in most cases was 3:2 of monomethyl itaconate:vinylpyridine repeat units. Complexes are insoluble in all the tested solvents; only fresh precipitate may be solubilized by increasing the pH of the solution. Complex formation is observed even when the density of pyridine groups is reduced to 25% by copolymerization with styrene. Differential scanning calorimetry analyses do not show a glass transition temperature for poly(monomethyl itaconate) polymer complexes; only a wide degradation peak was observed. Thermogravimetric experiments corroborate that the thermal degradation behaviour does not differ substantially from that of the pure components. In these conditions, Fourier-transform infra-red spectroscopy was used to study their hydrogen-bonding interactions. The infra-red spectra corresponding to polycomplexes clearly show evidence of hydrogen bonding between the components and there seems to be some evidence of partial pyridine protonation.

(Keywords: poly(vinylpyridine)s; poly(monomethyl itaconate); complex formation)

INTRODUCTION

Miscibility in polymer blends can be enhanced by specific interactions between the components. These interactions can give a negative enthalpy-of-mixing term in the Gibbs free-energy equation and, provided that entropic contributions are negligible for the polymer blends, the resultant Gibbs free energy is negative and mixing is thermodynamically possible (favourable). The majority of miscible polymer blends reported in the literature present specific interactions like charge transfer, acid–base complexation or hydrogen bonding.

In systems where specific interactions are rather strong, like blends of polyacids and polybases, interpolymer complexation may occur[1,2]. These types of materials usually show a physical behaviour quite different from that of the pure components, and they have interesting applications in a variety of fields like medicine, pharmacology or biology.

An interesting family of polybases with a great ability to develop interpolymer complexes with polyacids are the poly(vinylpyridine)s in their 2- and 4-isomer forms. These polymers form interpolymer complexes with poly(carboxylic acid)s like poly(acrylic acid)[3] and poly(ethylene-*co*-methacrylic acid)[4], and with other acids like poly(2-acrylamido-2-methylpropanesulfonic acid)[5] or poly(vinylphenol)[6].

Among the polyacids, poly(monoitaconate)s are compounds of particular interest because they can be obtained from biological monomers. These polymers show a chemical structure close to that of poly(acrylic acid) and poly(methacrylic acid), with a similar ability to develop interpolymer complexes with polybases like poly(vinylpyrrolidone)[7–12]. In this work we show that the first member of the group, poly(monomethyl itaconate), forms strong acid–base complexes with poly(2-vinylpyridine) and poly(4-vinylpyridine). The chemical structures of the three monomers are shown in *Figure 1*.

EXPERIMENTAL

Poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) samples were kindly supplied by Reilly Chemical Corp., and the polymers were purified by precipitation using the methanol/ethyl ether pair. The weight-average molar masses were determined by laser light scattering at 25°C using as solvents 1,4-dioxane for P2VP ($M_w = 53\,000\,\mathrm{g\,mol^{-1}}$, $\mathrm{d}n/\mathrm{d}c_2 = 0.137\,\mathrm{cm^3\,g^{-1}}$) and ethanol for P4VP ($M_w = 49\,000\,\mathrm{g\,mol^{-1}}$, $\mathrm{d}n/\mathrm{d}c_2 = 0.210\,\mathrm{cm^3\,g^{-1}}$).

4-Vinylpyridine-*co*-styrene copolymers were synthesized by radical polymerization at 75°C under N_2

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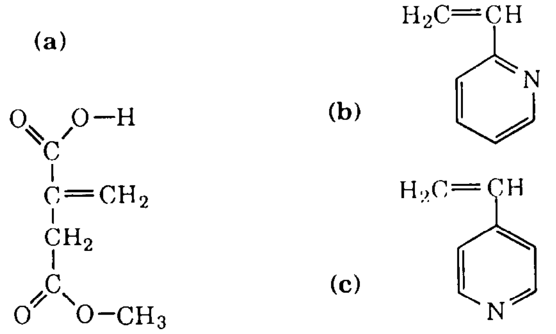

Figure 1 Chemical structures of (a) monomethyl itaconate, (b) 2-vinylpyridine and (c) 4-vinylpyridine

atmosphere. Toluene was used as solvent (50% w/w) and azobisisobutyronitrile (AIBN) as initiator[6]. For preparing the blends, two different compositions (P4VP/PS 50/50 and 25/75) were selected.

Monomethyl itaconate was synthesized by the esterification of itaconic acid (1 mol) with methanol (3 mol), using freshly distilled acetyl chloride as catalyst.

Poly(monomethyl itaconate) (PMMI) was obtained by bulk-free radical polymerization using AIBN as initiator under N_2 atmosphere at 80°C. We chose this polymerization method because it allowed us to obtain a greater yield than obtained when using reported methods[13]. This polymer was characterized by laser light scattering in methanol solution, at 25.0°C. A weight-average molar mass of 92 000 g mol^{-1} was obtained ($dn/dc_2 = 0.144\,cm^3\,g^{-1}$).

The complexes were prepared by mixing solutions of PMMI and poly(vinylpyridine)s (2% w/v in methanol). Since the sequence of addition would influence the complex formation[9], in all cases the P2VP or P4VP solutions were added to the PMMI ones. After four days (to assure thermodynamic equilibrium conditions), the precipitates were separated by centrifugation, washed with methanol and dried under vacuum for three days at 65°C (to assure total elimination of the solvent). There are few common solvents for PMMI and poly(vinylpyridine)s; in fact we have found only two, methylformamide and methanol. With methylformamide the results obtained are quite similar to those found with methanol, although the former solvent can be considered as a strong proton acceptor and thus it is able to compete with poly(vinylpyridine)s for acid PMMI sites. Several binary mixtures of methanol with water, dimethylformamide (DMF), dimethylacetamide (DMAc) and tetrahydrofuran (THF) were prepared. In all cases, instantaneous precipitate formation was observed after mixing the solutions of PMMI and P4VP (or P2VP) in these binary solvents.

The calorimetric analyses of complexes were carried out using a Mettler TA4000 differential scanning calorimeter and a Mettler TG50 thermobalance. In all cases the weight of samples was about 8 mg and scanning speed was 10°C min^{-1}. The analyses were carried out under N_2 atmosphere (200 cm^3 min^{-1}).

Infra-red spectra were recorded on a Nicolet-520 Fourier-transform infra-red (*FT*i.r.) spectrophotometer with a resolution of 1 cm^{-1} and were averaged from 200 scans. Samples for *FT*i.r. measurements were prepared by dispersing the blends into potassium bromide discs. High-temperature experiments were performed using a Specac variable-temperature cell P/N 21500 with a Eurotherm 847 temperature unit controller coupled to the spectrophotometer. The spectra were recorded when the chosen temperature was reached using a scan speed of 5°C min^{-1}. The selected temperatures were 25, 80, 100, 120, 140, 160, 180 and 200°C.

RESULTS AND DISCUSSION

When methanolic solutions of PMMI and P4VP (or P2VP) are mixed together, a white gelatinous precipitate readily forms. This precipitate, independently of the solution temperature, remains stable. It was possible to obtain a precipitate starting with solutions as dilute as 0.01% w/w. When the precipitate is isolated by centrifugation (1 h at 5000 r.p.m.), and the solvent is eliminated under vacuum at room temperature, we found that the formed complex is not soluble in the solvents commonly used to dissolve these polymers (e.g. methanol, methylformamide, etc.). We have not yet found any solvent that can redissolve the precipitate obtained in this way. Only fresh precipitate may be solubilized by increasing the pH of the solution. The complexes can be reprecipitated by lowering the pH of the solution. All these facts indicate the formation of PMMI–P4VP and PMMI-P2VP polycomplexes from methanolic solutions and suggest strong specific interactions between the components.

The influence of solvent medium in the complex formation was studied because it can play an important role in the control of the specific interactions between the components. In particular, if the solvent has a strong acid or basic character, it may compete with the polymeric components, interacting with donor or acceptor sites, and thus avoiding complex formation[6,12,14]. The results obtained with other solvents (methylformamide, and several binary mixtures of methanol with water, DMAc, DMF and THF) show that there is a high degree of selectivity in the specific interactions leading to polycomplex formation.

Another way of decreasing the number of specific interactions is to reduce the density of the sites responsible. For this reason, several styrene-*co*-4-vinylpyridine copolymers were synthesized. We found that, for the copolymers with 50% pyridine units, their mixtures with PMMI from methanolic solutions lead to complex formation. When the content in pyridine units is 25%, the mixtures of these copolymers with PMMI using the binary solvent methanol/THF 50/50 (methanol is not a solvent of this copolymer) lead to complex formation too. We can conclude that the interactions involved in these systems are very strong and with a high degree of specificity.

It is possible to determine the composition of PMMI–poly(vinylpyridine) complexes by elemental analysis, because the repeat unit in vinylpyridine polymers has a nitrogen atom that is not present in the PMMI. All the samples studied by this method were prepared from methanolic solutions using a procedure similar to that described in the 'Experimental' part. The data obtained by elemental analysis are shown in *Table 1*. Composition of complexes has been calculated taking the C/N ratios for the different samples. Some interesting facts can be pointed out from these data. The PMMI : poly(vinylpyridine) molar ratio of repeat units

Table 1 Elemental analysis for poly(vinylpyridine)s and polymer–polymer complexes obtained at different feed compositions

Sample	C (%)	N (%)	H (%)	PMMI : PVP ratio ± 0.2	PMMI : PVP
PMMI (theoretical)	50.0	–	5.6	–	–
PMMI	45.7	–	5.7	–	–
P2VP (theoretical)	80.7	13.5	5.8	–	–
P2VP	77.3	12.9	6.9	–	–
P2VP/PMMI 20/80	46.0	3.6	5.3	1.41	3 : 2
40/60	50.8	3.7	6.0	1.62	3 : 2
60/40	52.6	4.3	6.0	1.30	3 : 2
80/20	56.7	5.6	6.2	0.85	1 : 1
P4VP (theoretical)	80.7	13.5	5.8	–	–
P4VP	76.9	12.9	6.5	–	–
P4VP/PMMI 20/80	49.6	3.2	6.3	1.97	2 : 1
40/60	51.4	3.9	6.4	1.48	3 : 2
60/40	49.1	3.5	6.1	1.70	3 : 2
80/20	51.0	5.2	6.3	0.79	1 : 1

of the complexes is quite simple and, in all cases, the stoichiometry was rounded to the closest integer values within experimental error. For PMMI–P4VP and PMMI–P2VP complexes, the obtained stoichiometry corresponds to a 3 : 2 molar ratio of PMMI : poly(vinylpyridine) repeat units. Only for the complexes obtained from solutions with lower content of PMMI and for a feed composition of 20% P4VP, was a change in the molar ratio observed. Simple molar ratios in polymer–polymer complexes have previously been reported for other systems[1,2,12,14,15].

From the results obtained it is not possible to conclude that the PMMI and poly(vinylpyridine)s form complexes with the same stoichiometry. In order to get a better understanding of the complex formation it is necessary to determine the phase diagram of the ternary system methanol/PMMI/poly(vinylpyridine). Djadoun *et al.*[16] have reported phase diagrams for ternary systems, involving similar polyacid/polybase interacting units, that indicate the stoichiometry dependence on concentration.

Another important topic in the characterization of polymer–polymer complexation is the study of the amount of polycomplex obtained as a function of feed composition. The amount of complex formed as a function of the PMMI composition in the feed is shown in *Figure 2*. Higher yields are obtained with a feed rich in PMMI, and yield decreases sharply as the content of P4VP or P2VP increases. For both systems, maximum yield is obtained for feed compositions around 30% in weight of poly(vinylpyridine) corresponding to a 3 : 2 molar ratio of PMMI:poly(vinylpyridine) repeat units. This behaviour is in good agreement with the elemental analysis results. Except for a poly (vinylpyridine) feed composition below 20%, the obtained yields are higher in the system PMMI–P4VP than in the PMMI–P2VP one (see *Figure 2*). Data in *Figure 2* suggest a greater ability of P4VP than P2VP for complex formation. This different hydrogen-bonding ability for P4VP and P2VP has also been found in strong hydrogen-bonded blends[17–19].

Calorimetric analysis

We have performed d.s.c. analyses in the temperature range of −25 to +250°C. As is displayed in *Figure 3*, P2VP and P4VP exhibit a well defined glass transition (100 and 148°C, respectively), whereas the thermal behaviour of PMMI is rather different. As has been pointed out by Cowie *et al.*[20], this polymer does not exhibit a glass transition temperature. On the other hand, we must emphasize that the thermal behaviour of PMMI strongly limits the scope of our calorimetric analyses. Calorimetric curves of PMMI show a pronounced slope beginning from moderate temperatures (40°C) in addition to a wide endothermic peak located near 145°C. The position of this endothermic peak coincides with the onset of thermal degradation processes in the polymer, as we have confirmed by thermogravimetric analysis. This thermal behaviour makes difficult our studies above 40°C, and for this reason it is necessary to take special care in the thermal treatments of PMMI.

The most relevant characteristic in the thermal curves of our polymer complexes (more for PMMI–P4VP than for PMMI–P2VP systems) is the absence of any glass transition process at temperatures under 120°C. The lack of this type of process is not surprising considering that we are working with strong hydrogen-bonded materials, as is proved in this paper from the infra-red spectra. Under these conditions, intermolecular hydrogen bonding acts like physical crosslinking, increasing the glass transition temperature of the material. This is a typical behaviour in polymer–polymer complexes and in

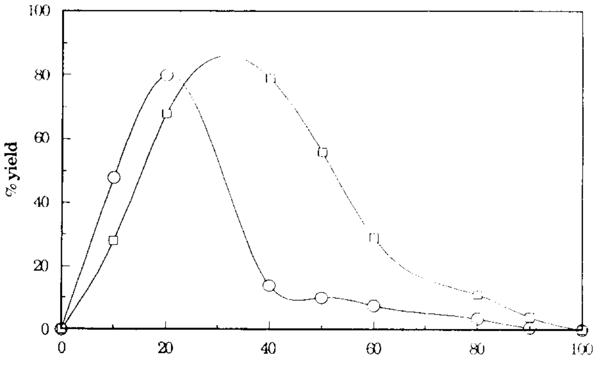

Figure 2 Yield of complex formation at different feed compositions for: (○) PMMI–P2VP and (□) PMMI–P4VP

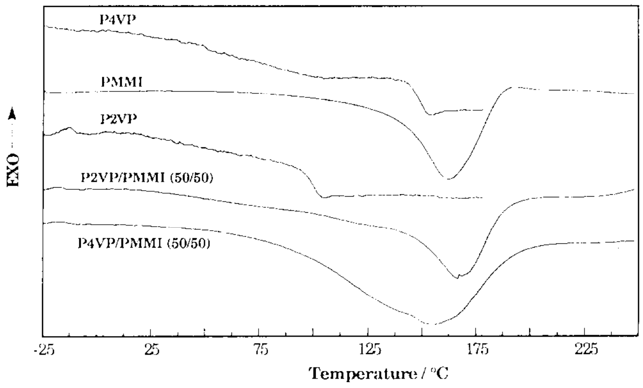

Figure 3 Scaled d.s.c. curves for pure components and complexes at 1:1 feed composition

strongly associated polymer blends[15,21]. Thus, it is possible that, if these hypothetical glass transition processes take place, they occur at temperatures where thermal degradation of the sample has already started, masking its calorimetric detection. The wide endothermic peak is observed in all the studied complexes (*Figure 3*).

Thermogravimetric analyses show important differences between the thermal degradation behaviour of the pure components and that of the polymer–polymer complexes. We have already pointed out the weak thermal stability of PMMI compared with that of the poly(vinylpyridines). PMMI thermogravimetric curves show a first degradative process starting at 145°C and ending at 210°C. Above this temperature there are some other degradation processes that become especially important (below 280°C). The first process has been attributed to the formation of cyclic and linear anhydrides[20], with loss of water and methanol. At high temperature, decarboxylation processes (loss of CO_2 molecules) also seem to play an important role. This is a frequent process in other polyacids with chemical structures close to PMMI such as poly(acrylic acid)[22] and poly(methacrylic acid)[23].

Poly(vinylpyridine)s are thermally stable polymers, without significant differences between the 2- and 4-isomers. In both polymers there is no substantial mass loss under 300°C ($\approx 4\%$), and thermal degradation processes start at about 350 and 380°C for P4VP and P2VP, respectively. Thus, the thermal degradation behaviour of PMMI and poly(vinylpyridine)s is quite different.

Thermogravimetric curves of complexes show some remarkable facts. As can be seen in *Figure 4*, we found that there are some significant differences between the thermal degradation behaviour of PMMI–P4VP and PMMI–P2VP complexes. However, we must point out that both interpolymer complexes show a thermal degradation behaviour that does not depend strongly on their feed compositions.

For PMMI–P2VP complexes, the first degradative process takes place in the range ≈ 160–200°C, with a mass loss close to 15% for all the studied feed compositions. After several minor degradative processes, a higher mass loss takes place at about 350°C. The thermal degradation of PMMI–P4VP complexes starts in the same range ≈ 160–200°C (12% mass loss), then an important second process starts at about 275°C up to 320°C, with a loss of mass of around 20%.

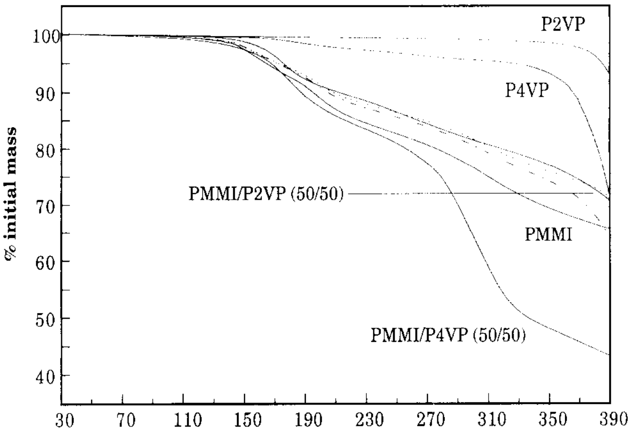

Figure 4 Thermogravimetric curves for pure components and complexes at 1 : 1 feed composition: (·····) theoretical thermogram of PMMI–P2VP complex with a 3 : 2 stoichiometry; (—-—) theoretical thermogram of PMMI–P4VP complex with a 3 : 2 stoichiometry

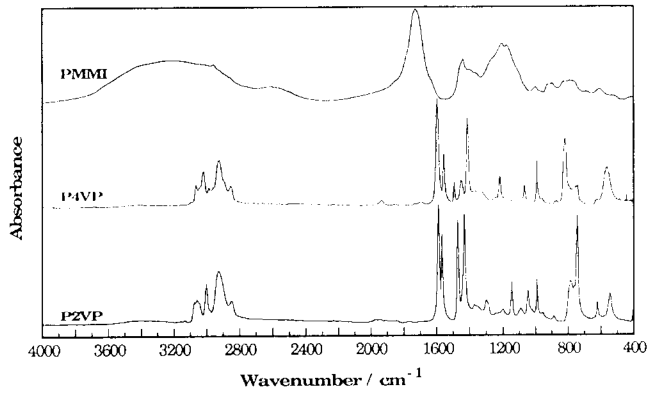

Figure 5 Infra-red spectra for pure components

The first thermal degradative process starts in polycomplexes at higher temperatures than those of pure PMMI. In this way, poly(vinylpyridine)s have a stabilizing effect, probably due to the extensive hydrogen bonding in the complexes, which retards anhydride formation in PMMI carboxylic groups. In *Figure 4*, the 'theoretical' and experimental thermogravimetric curves are shown. These 'theoretical' curves have been calculated as the sum of the thermogravimetric curves of the two unmixed materials, using a stoichiometry equal to 3:2 PMMI:poly(vinylpyridine). As can be seen in *Figure 4*, PMMI–P2VP complexes exhibit a degradative behaviour close to that predicted (obviously, with the exception of the initial retarding degradation effect commented upon above), whereas a strong shift from the additive behaviour is observed in PMMI–P4VP complexes. These facts suggest that in these complexes the degradation process of P4VP is enhanced. A similar behaviour has been reported for blends of P4VP with other poly(mono-n-alkyl itaconates)[24].

Fourier-transform infra-red analysis

To elucidate the i.r. spectra of the polycomplexes it is necessary to give a description of the main spectral features of their pure components. The infra-red spectrum of PMMI is dominated by the characteristic bands attributed to associated polyacids, although with some singularities. The hydroxyl stretching region in PMMI spreads from 3100 to 3650 cm^{-1}, as displayed in

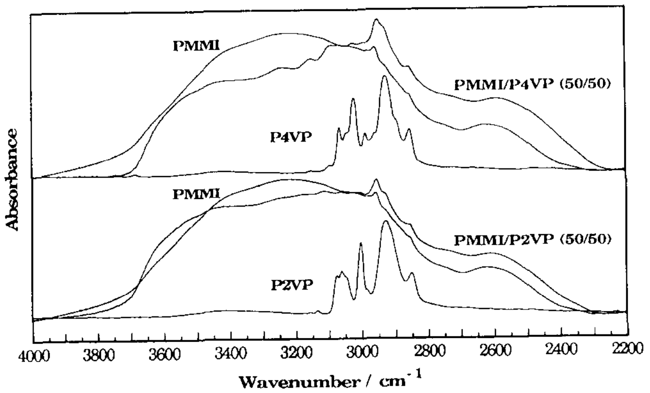

Figure 6 Infra-red spectra in the 2200–4000 cm^{-1} region for pure components and complexes at 1 : 1 feed composition

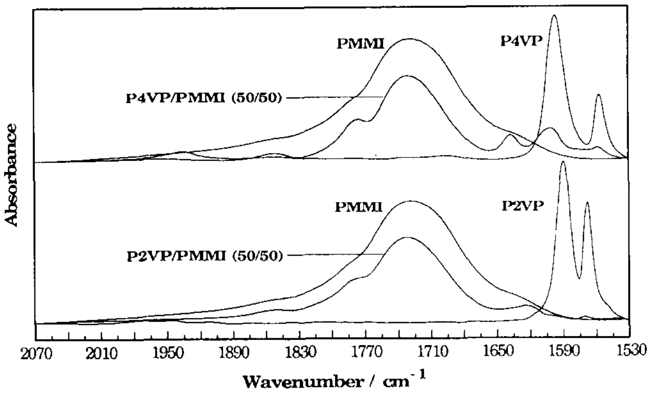

Figure 7 Infra-red spectra in the 1530–2070 cm^{-1} region for pure components and complexes at 1 : 1 feed composition

Figure 5. We can notice a contribution due to nonbonded hydroxyl groups (shoulder at 3600 cm^{-1}) together with a contribution due to associated hydroxyl groups under different forms. The band width and its position suggest that dimerization is not the principal way of self-association in PMMI (typical band[25] placed at 3100 cm^{-1}). Also remarkable is the presence of a weak satellite band centred at 2615 cm^{-1}, attributable to associated hydroxyl groups.

PMMI shows a rather complicated carbonyl stretching spectral region. Thus, we found a wide carbonyl band located from 1650 to 1890 cm^{-1}, and centred at about 1725 cm^{-1}. Because of the chemical structure of PMMI, we can expect that the main contributions to this complex band are: carbonyls in carboxyl groups, in both non-associated and associated (hydrogen-bonding) forms; and carbonyls from ester groups, again associated or non-associated. As minor contributions, we must point out the presence of weak shoulders at 1780 and 1855 cm^{-1} attributable to cyclic anhydrides formed during the polymerization process[26]. The shoulder at 1640 cm^{-1} could be due to residual monomer. However, spectra obtained at high temperature, after thorough purification of the polymer, still showed this band. This fact supports the hypothesis that this band is due to diketone structures formed in the polymerization process, as has been reported by Tate for poly(itaconic acid)[27].

The infra-red spectra of poly(vinylpyridine)s have been previously described[4] and the most remarkable bands are the characteristic modes of the pyridine ring at 1590, 1050 and 993 cm^{-1} for P2VP and at 1597, 1493 and 993 cm^{-1} for P4VP.

The infra-red spectra corresponding to polycomplexes clearly show evidence of hydrogen bonding between the components. We found important modifications in the hydroxyl stretching modes of PMMI and pyridine ring modes of P4VP and P2VP in the complexes. First, as can be seen in *Figure 6*, the hydroxyl stretching region shows an increase of the contribution at wavenumbers higher than those corresponding to dimers. This effect is particularly important in the polycomplexes formed by P4VP. On the other hand, we found a remarkable spectral shift of the satellite band towards low wavenumber, about 31 cm^{-1} for PMMI–P4VP complexes and 12 cm^{-1} for PMMI–P2VP ones.

Another remarkable fact related to these spectral modes is the increase of the weak band at about 1950 cm^{-1} (see *Figure 7*); this band has been previously reported by Lee *et al.*[4] in P2VP–poly(ethylene-*co*-methacrylic acid) complexes and has been attributed to overtones or combinations of the stretching modes O–H and H–N (hydrogen bonded). Again, the intensity of this band is higher in PMMI–P4VP than in PMMI–P2VP complexes.

The characteristic pyridine spectral ring modes also undergo modifications, attributable to hydrogen-bonded pyridine rings. Those corresponding to pyridine spectral modes placed at higher wavenumber are of analytical interest, because the rest are overlapped with PMMI bands. In *Figure 7* is displayed the infrared spectrum of one of the PMMI–P4VP and one of the PMMI–P2VP complexes. A shift of the 1597 cm^{-1} band towards higher wavenumbers can be observed. This shift is approximately 6 cm^{-1} and, according to our results (see *Table 2*), it does not seem to be dependent on feed composition of the prepared complexes. Similar conclusions are made for P2VP complexes; the band located at 1590 cm^{-1} shows a more important shift, approximately 10 cm^{-1} (*Table 2*). An important question to take into account is the strength of this interaction. Rego and Huglin[5], in their study of poly(vinylpyridine)–poly(2-acrylamido-2-methylpropanesulfonic acid), found formation of effective crosslinking and, thus, complete pyridine protonation. Lee *et al.*[4] report hydrogen bonds of intermediate strength and partial protonation in P2VP–poly(ethylene-*co*-methacrylic acid). In our complexes there seems to be some evidence of partial pyridine protonation. A detailed inspection of P4VP–PMMI i.r. spectra shows a weak band around 1638 cm^{-1} that can be attributed to protonated pyridine rings. This band has been previously reported for ionic blends of sulfonated polystyrene and

Table 2 Wavenumbers of pyridine ring modes in the PMMI–P2VP and PMMI–P4VP polymer–polymer complexes for different feed compositions

P2VP (wt%)	1590 cm^{-1} band shifted to	P4VP (wt%)	1597 cm^{-1} band shifted to
20	1600	20	1604
40	1600	40	1603
50	1601	50	1603
60	1600	60	1603
80	1600	80	1602
100	1590	100	1597

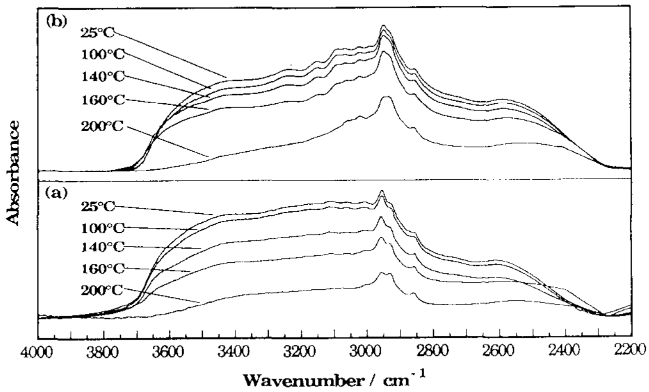

Figure 8 Infra-red spectra in the 2200–4000 cm^{-1} region at different temperatures: (a) PMMI–P2VP complex at 1:1 feed composition and (b) PMMI–P4VP complex at 1:1 feed composition

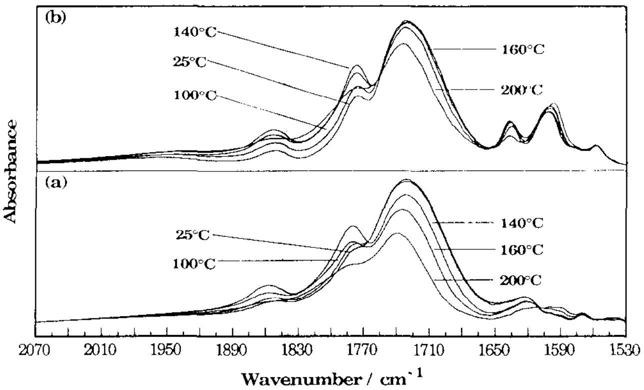

Figure 9 Infra-red spectra in the 1530–2070 cm^{-1} region at different temperatures: (a) PMMI–P2VP complex at 1:1 feed composition and (b) PMMI–P4VP complex at 1:1 feed composition

poly(ethyl acrylate-*co*-4-vinylpyridine)[28], and it is also usual in the spectra of lower-molar-mass analogues, like complexes of pyridine with acids[29]. For P2VP–PMMI complexes a similar band is located at 1624 cm^{-1}. In conclusion, it seems that partial protonation of poly(vinylpyridine)s takes place in these complexes.

The carbonyl stretching band of the complexes also shows some differences from the band shape observed in pure PMMI. This band is narrower in the complexes than in pure PMMI. Narrowing may be attributed to a change in the hydrogen-bonding distribution for the system. The modifications in the hydroxyl stretching and pyridine ring bands suggest an increase of carboxyl–pyridine hydrogen bonding at the expense of carboxyl–carboxyl and carboxyl–carbonyl (ester and anhydride) ones; consequently the reduction of this last type of contribution leads to a narrowing of the carbonyl band.

Finally, we have performed a study of the infra-red spectra of the complexes as a function of temperature, in the range of 25 to 200°C. The experiments have been performed at a scan speed of 5°C min^{-1}, keeping the selected temperature constant to record the spectra. Some interesting facts are observed in the spectra, which are displayed in *Figure 8*. First, we can clearly observe some phenomena related to hydrogen-bond breaking. For instance, the shoulder in the hydroxyl stretching band at 3600 cm^{-1}, attributable to non-bonded hydroxyl groups, becomes more intense as sample temperature rises. On the contrary, the overtone corresponding to acid dimers decreases in intensity with temperature. This effect could be due to the loss of hydroxyl groups by anhydride formation in PMMI.

The carbonyl stretching region is also affected by the thermal treatment. For temperatures above 120°C, an important increase in the contribution of cyclic anhydride bands is observed in *Figure 9*. There is an important reduction in the absorbance of the bands corresponding to the other types of carbonyl groups and a narrowing of this complex band. These results are in agreement with the thermal degradation measurements of PMMI. This polymer exhibits cyclic anhydride formation above 120°C, and at higher temperatures (≈ 160°C) decarboxylation processes also take place. In both cases there is a loss of carbonyl groups and consequently we can expect a reduction in the absorbance of the carbonyl band.

Thermogravimetric results indicate slight differences in the onset degradation temperatures between PMMI and the complexes. According to the i.r. results, this effect does not seem to modify the degradative mechanism of this component in the complexes at temperatures below 200°C.

CONCLUSIONS

*FT*i.r. measurements show that PMMI and poly(vinylpyridine)s form hydrogen-bonded polymer–polymer complexes. These interactions are very selective and, with only a minor content of pyridine units in copolymers with styrene, instantaneous complex formation is observed. Taking into account that we have not found a solvent for PMMI–poly(vinylpyridine) complexes, we can conclude that the extent of hydrogen bonding must be large. For this reason, a polymer chain must be linked with others forming a packed lattice.

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REFERENCES

1 Bekturov, E. A. and Bimendina, L. A. *Adv. Polym. Sci.* 1981, **41**, 99
2 Tsuchida, E. and Abe, K. *Adv. Polym. Sci.* 1982, **45**, 1
3 Piérola, I. F., Cáceres M., Cáceres, P., Castellanos, M. A. and Núñez, J. *Eur. Polym. J.* 1988, **24**, 895
4 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 954
5 Huglin, M. B. and Rego, J. M. *Polymer* 1990, **31**, 1269
6 Vivas de Meftahi, M. and Fréchet, J. *Polymer* 1988, **29**, 477
7 Bimendina, L. A., Bekturov, E. A., Tleubaeva, G. S. and Frolova, V. A. *J. Polym. Sci., Polym. Symp.* 1979, **66**, 9
8 Anasagasti, M., Valenciano, R., Rivas, I. and Katime, I. *Polym. Bull.* 1982, **28**, 669
9 Pérez-Dorado, A., Piérola, I. F., Baselga, J. and Radic, D. *Makromol. Chem.* 1989, **190**, 2975

10 Pérez-Dorado, A., Piérola, I. F., Baselga, J. and Gargallo, L. *Makromol. Chem.* 1990, **191,** 2905

11 Cesteros, L. C., Rego, J. M., Vazquez, J. J. and Katime, I. *Polym. Commun.* 1990, **31,** 152

12 Cesteros, L. C., Meaurio, E. and Katime, I. *Polym. Int.* 1994, **34,** 97

13 Yang, J. Z. and Otsu, T. *Polym. Bull.* 1991, **25,** 145

14 Yang, T. P., Pearce, E. M., Kwei, T. K. and Yang, N. L. *Macromolecules* 1989, **22,** 1813

15 Wang, L. F., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci. (B) Polym. Phys.* 1991, **29,** 619

16 Djadoun, S., Goldberg, R. N. and Morawetz, H. *Macromolecules* 1977, **10,** 1015

17 Moore, J. A. and Kim, J. H. *Macromolecules* 1992, **25,** 1427

18 Cesteros, L. C., Isasi, J. R. and Katime, I. *J. Polym. Sci. (B) Polym. Phys* 1994, **32,** 223

19 Cesteros, L. C., Meaurio, E. and Katime, I. *Macromolecules* 1993, **26,** 2323

20 Cowie, J. M. G. and Haq, Z. *Brit. Polym. J.* 1977, **9,** 241

21 Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn.* 1984, **22,** 307

22 Maurer, J. J., Eustace, D. J. and Ratcliffe, T. *Macromolecules* 1987, **20,** 196

23 Ho, B. C., Lee, Y. D. and Chin, W. K. *J. Polym. Sci. (A) Polym. Chem.* 1992, **30,** 2389

24 Cesteros, L. C., Velada, J. L. and Katime, I. *Polymer* 1995, **36,** 2765

25 Bellamy, L. J. 'The Infrared Spectra of Complex Molecules' 2nd Edn., Chapman & Hall, London, 1980, Vol. II

26 Nagai, S. and Fujiwara, F. *J. Polym. Sci, Polym. Lett. Edn.* 1969, **7,** 177

27 Tate, B. *Makromol. Chem.* 1967, **109,** 176

28 Sakurai, K., Douglas, E. P. and MacKnight, W. J. *Macromolecules* 1992, **25,** 4506

29 Takahashi, H., Mamola, K. and Plyler, E. *J. Mol. Spectrosc.* 1966, **21,** 217