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Highly interacting polymer blends: poly(monoethyl itaconate)/ poly(vinylpyridine)s

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In this paper the interactions of poly(monoethyl itaconate) with poly(2-vinylpyridine) and poly-(4-vinylpyridine) have been studied. Polymer blends or polycomplexes can be obtained, depending on the solvent employed. The stoichiometry found for the polycomplexes obtained was 2:1 of monoethyl itaconate: pyridine repeat units. Polymer complexes do not show a standard glass transition temperature. On the contrary, blends involving poly(monoethyl itaconate) and poly(2-vinylpyridine) show a broad glass transition. The thermal degradation behaviours of complexes and blends do not differ substantially from those of the pure components. Fourier-transform infra-red spectroscopy was used to study the hydrogen-bonding interactions in complexes and blends.

(Keywords: poly(vinylpyridine)s; poly(monoethyl itaconate); blends)

INTRODUCTION

During the past years, the study of polymer blends as alternative materials has greatly expanded. Miscibility of polymer blends can only be achieved when the enthalpy of mixing is negative, since the entropic contribution to miscibility is negligible in these systems. Therefore, specific interactions at the molecular level will promote the formation of miscible polymer blends. A very high number of specific interactions between the components should lead to the formation of polymer–polymer complexes. For instance, the mixing of polyacid and polybase solutions can produce, under given conditions, interpolymer complexes stabilized through cooperative hydrogen bonding between the acidic and basic groups[1–6]. The nature of the resulting material can be controlled by varying the feed composition, the solvent employed or the temperature.

In another paper[5], we report the polymer–polymer complexation between poly(monomethyl itaconate) and poly(vinyl pyridine)s. Now we extend this study to the materials obtained by mixing poly(monoethyl itaconate) (PMEI) with poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP).

These new systems have several points of interest. The more hydrophobic nature of PMEI compared to PMMI allows one to find a solvent capable of miscibility and polymer–polymer complexation. Accordingly, two types of materials can be obtained: (i) complexes that are prepared by mutual precipitation in a common solvent and (ii) blends that are obtained by evaporation. Complexes have a molecular composition imposed by the nature and extent of acid–base specific interactions, whereas blends have a composition similar to the original feed composition. P4VP and P2VP have a different capability for specific interactions with PMEI, and the comparison of the materials obtained from these two isomeric forms of poly(vinylpyridine) is a matter of interest.

This paper is aimed at elucidating the kind and number of specific interactions that occur between PMEI and poly(vinylpyridine)s as well as at comparing the thermal behaviour of both kinds of materials.

EXPERIMENTAL

Monoethyl itaconate (MEI) was synthesized by esterification of itaconic acid (1 mol) with ethanol (3 mol) using freshly distilled acetyl chloride as catalyst[7]. Poly(monoethyl itaconate) (PMEI) was obtained by bulk free-radical polymerization of MEI using azobisisobutyronitrile (AIBN) as initiator. The reaction takes place under N_2 atmosphere at 60°C for 2.5 h. PMEI was purified by successive precipitation in a 50/50 vol% methanol/ethyl ether mixture and subsequently by solid–liquid extraction in a Soxhlet apparatus using dichloromethane as solvent. The resultant polymer was characterized by laser light scattering in methanol at 25°C ($dn/dc = 0.130\,cm^3\,g^{-1}$). The obtained weight-average molar mass was $225\,000\,g\,mol^{-1}$.

Poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) samples were kindly supplied by Reilly Chemical Corp. Molar masses were determined by viscometry, using pyridine as solvent for P2VP ($[\eta] = 13.8 \times 10^{-3} M^{0.69}$) and ethanol for P4VP ($[\eta] = 2.5 \times 10^{-3} M^{0.68}$). The corresponding molar masses were 46 000 and $33\,000\,g\,mol^{-1}$, respectively. Both P2VP and

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P4VP were purified by successive precipitation in a methanol/ethyl ether mixture before use. The chemical structures corresponding to the three polymers studied here are shown in *Figure 1*.

Polymer–polymer complexes were prepared from ethanol solutions (2% w/v) of PMEI and poly(vinylpyridine)s. P2VP or P4VP solutions were added to PMEI ones. Complete complexation was ensured by leaving the different systems at room temperature for four days. This time interval was found to be adequate for this purpose by gravimetric analysis of precipitates before the actual experiments. After this stabilization time, the precipitates were separated from the solvent by centrifugation at 5000 r.p.m., washed with methanol and dried under vacuum for three days at 65°C to ensure total elimination of the solvent.

Polymer–polymer blends were prepared from 2% w/v pyridine solutions of PMEI and poly(vinylpyridine)s by mixing the P2VP or P4VP solutions with the PMEI ones. Blends were obtained by solution casting of the mixture prepared. The final drying step took place in a vacuum desiccator for three days at 65°C.

Thermal analyses of complexes were done with a Mettler TA4000 differential scanning calorimeter and a Mettler TG50 thermobalance. Sample weights varied from 8 to 10 mg; scan speed was 10 or 20°C min^{-1}. Thermogravimetric analyses were carried out under N_2 atmosphere (200 ml min^{-1}).

Infra-red spectra were performed on solid samples in the form of potassium bromide pellets. The spectra were recorded on a Nicolet-520 Fourier-transform infra-red spectrophotometer with a resolution of 2 cm^{-1} averaging from 100 scans. 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.

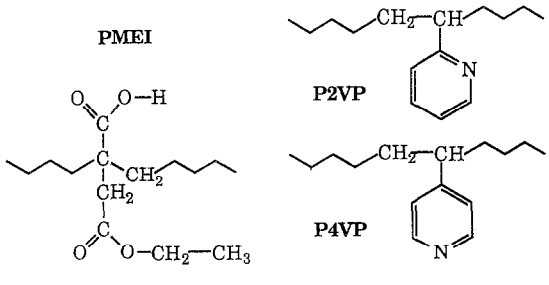

Figure 1 Chemical structure of PMEI, P2VP and P4VP

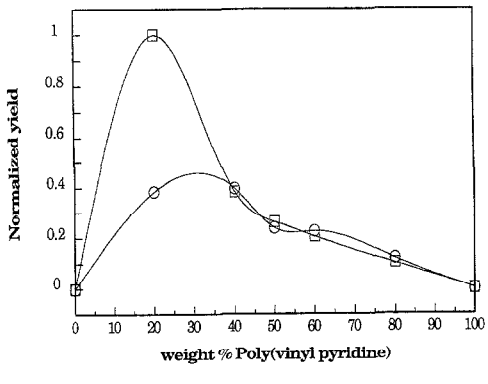

Figure 2 Polycomplex formation yield for PMEI–P2VP (○) and PMEI–P4VP (□)

RESULTS AND DISCUSSION

When methanolic solutions of PMEI are mixed with methanolic solutions of P2VP or P4VP, white gelatinous precipitates are observed instantaneously. This solid formation is independent of the starting solution concentration; precipitates are observed even for very dilute solutions (10^{-4} g cm^{-3}) and develop whatever the mixture ratio of the employed methanolic solutions. The stability of the solid formed is independent of time and temperature. On the other hand, if the precipitate is isolated by centrifugation, removal of supernatant liquor and subsequent drying under vacuum, the polymer–polymer complex is found not to be soluble in common solvents of both homopolymers. The only way the precipitate obtained can be solubilized is to modify the solution pH when the precipitate is in the gel form.

Accordingly, the precipitation of polymer–polymer complexes from a common solvent, in which both polymers were initially soluble, is a manifestation of the more favourable attraction between the two different polymers than between polymer–solvent pairs. Similar results have been reported for PMMI–P2VP and PMMI–P4VP pairs[5].

The great influence of the solvent medium in the control of complex formation is well known. A solvent with a strong acidic or basic character may compete with the polymeric components to interact with donor or acceptor sites, thus avoiding complex formation[3,8–10]. Thus, other common solvents for PMEI and poly(vinylpyridine)s such as tetrahydrofuran (THF), dimethylformamide (DMF) or pyridine have been used here. Both THF and methanol show the same behaviour. The other two solvents can be considered as strong proton acceptors, and thus they can compete with poly(vinylpyridine)s for acidic PMEI sites. Precipitates are not observed in the PMEI–P2VP system when DMF is employed as solvent. In this case, the individual polymer solutions remain stable with time. A precipitate appears instantaneously when DMF solutions of PMEI and P4VP are mixed. This behaviour indicates that P4VP–PMEI interactions are more favourable than the P2VP–PMEI ones in the DMF medium. This could be attributed to a minor steric effect in the P4VP sites. This behaviour has been confirmed in other polymer blends[11–13]. Using pyridine as solvent, no precipitates are observed either with the PMEI–P2VP pair or with the PMEI–P4VP one. Pyridine allows one to obtain a true solution of both polymers and, therefore, a film of the blend with a known composition can be prepared by solvent casting.

This behaviour enables one to study two different classes of materials: those obtained by mutual precipitation from methanolic solutions, which will be named 'complexes', and those obtained by solvent casting from pyridine solutions, which will be named 'blends'. Blends can be prepared at controlled compositions, but complexes have a composition imposed by the cooperative specific interactions in the solution. It should be noted that no common solvent for PMMI and poly(vinylpyridine)s capable of inhibiting complex formation could be found. Accordingly, the systems reported in this paper are of interest from this point of view.

With regard to complexes, the yield of complex

Table 1 Elemental analyses data for several PMEI–P2VP and PMEI–P4VP polycomplexes

Sample	C (%)	H(%)	N (%)	PMEI : poly(vinylpyridine) molar ratio
P2VP	77.3	6.9	12.9	
PMEI/P2VP 80/20	58.7	6.5	3.4	2 : 1
60/40	54.1	6.8	0.9	9 : 1
40/60	54.7	6.8	1.2	7 : 1
20/80	55.9	6.6	2.1	7 : 2
P4VP	76.9	6.5	12.9	
PMEI/P4VP 80/20	58.9	6.6	3.4	2 : 1
60/40	54.1	6.7	1.0	8 : 1
40/60	53.8	6.5	0.8	10 : 1
20/80	55.5	6.6	1.9	4 : 1

formation depends on the feed composition of the precursors. *Figure 2* shows the complex formation yield as a function of the precursor feed composition (complex formation yields have been normalized to the maximum of these values). As can be seen from this figure, yield decreases dramatically as the content of PMEI in the feed composition decreases. The complex formation yield presents a maximum at a polymer feed composition in the range between 20 and 30% by weight of poly(vinylpyridine). The composition of these complexes can be determined by elemental analysis[5]. The results obtained by this method are given in *Table 1*. As can be observed from this table, a variety of materials with a broad distribution of compositions are obtained; a high content of monoethyl itaconate units, especially at feed compositions rich in poly(vinylpyridine), is noticeable. These results suggest that one poly(vinylpyridine) chain is probably linked to several PMEI chains. These results are different from the previously reported PMMI–poly(vinyl-pyridine) complexes, which exhibit an almost constant molar composition ratio of 2 : 1 of repeat units for different feed compositions. It is noteworthy that PMEI–poly(vinylpyridine) complexes corresponding to the maximum yield (20 wt% of poly(vinylpyridine)) also present a molar composition ratio of 2 : 1 of monoethyl itaconate : pyridine repeat units. Accordingly, the stoichiometry 2 : 1 seems to be the most preferred complex composition in both systems.

It is also relevant to note that the yield obtained for the system PMEI–P4VP at a composition of 20 wt% in poly(vinylpyridine) is much larger than that reached by the system PMEI–P2VP in the same compositions. This fact also indicates a greater ability of P4VP than of P2VP for complex formation. Finally, the results obtained with feed compositions different from 20 wt% of poly(vinylpyridine) are similar for both pairs of polymers.

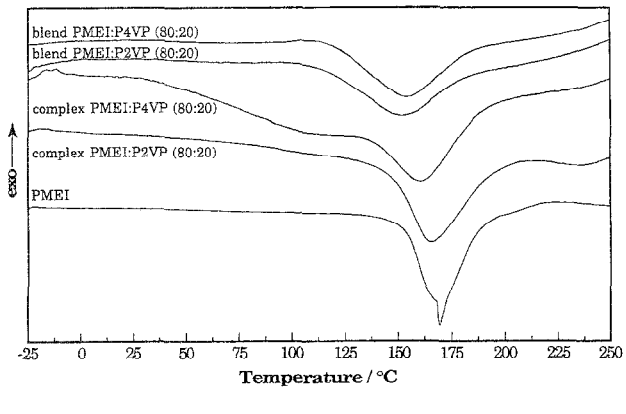

Figure 3 D.s.c. curves for PMEI and several PMEI–poly(vinylpyridine) systems

Table 2 Glass transition temperature for PMEI–P2VP blends

P2VP weight fraction	0.2	0.4	0.5	0.6	0.8
T_g (°C)	–	73	76	80	88

Calorimetric analysis

P2VP and P4VP show well defined glass transitions at 100°C and 148°C respectively. The thermal behaviour of PMEI is rather different (see *Figure 3*). This polymer does not exhibit a process that could be identified with a glass transition up to the degradation temperature[14,15]. The calorimetric curve of PMEI is dominated by a wide endothermic peak centred at 173°C. This temperature coincides with the maximum activity of the first degradation process, as can be observed from thermogravimetric analysis. The degradation of PMEI at relatively low temperature complicates the thermal studies at temperatures over 150°C. This fact should be taken into account during thermal treatments of PMEI, complexes and blends, since thermal behaviour could be altered differently, making the thermal results difficult to explain.

The thermal behaviour of our polymer complexes is totally marked by the tendency explained for PMEI. In both systems, PMEI–P2VP and PMEI–P4VP, the calorimetric curves follow the same form. There is no evidence of a defined glass transition at temperatures under 140°C. This behaviour is similar to that previously reported for PMMI–poly(vinylpyridine), and can be attributed to specific interactions[5]. All the complexes studied show a wide endothermic peak located around 161°C. It would appear from these results that poly(vinylpyridine)s promote the thermal degradation of PMEI at lower temperatures.

The calorimetric analysis of blends shows some differences with respect to the behaviour observed for

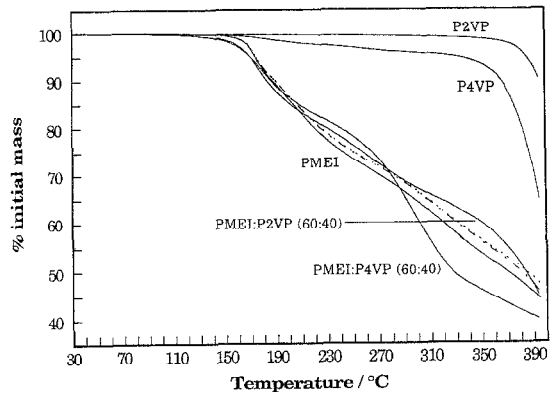

Figure 4 Thermogravimetric analyses for the homopolymers and two complexes: (·····) theoretical thermogram of PMEI–P2VP complex with a 10:1 stoichiometry; (–·–) theoretical thermogram of PMEI–P4VP complex with a 10:1 stoichiometry

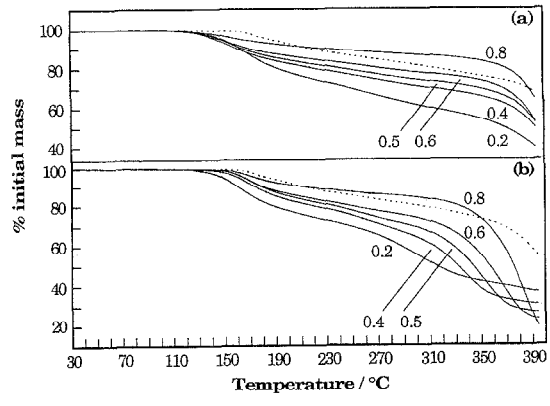

Figure 5 Thermogravimetric analyses. (a) PMEI–P2VP blends of several weight fractions; (·····) theoretical thermogram of PMEI–P2VP blend with P2VP weight fraction = 0.5. (b) PMEI–P4VP blends of several weight fractions; (·····) theoretical thermogram of PMEI–P4VP blend with P4VP weight fraction = 0.5.

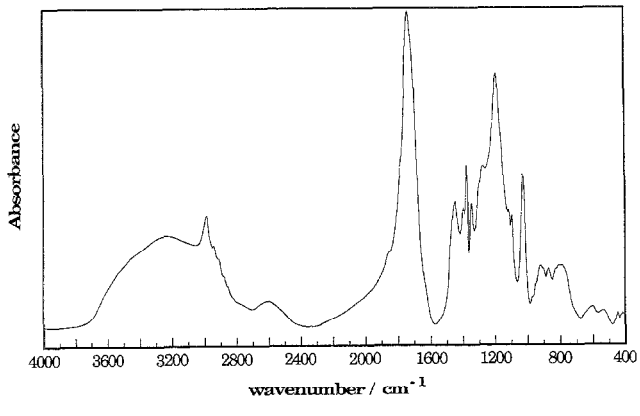

Figure 6 Scale-expanded infra-red spectrum for PMEI

the complexes. If the system PMEI–P2VP is considered, a broad glass transition appears around 80°C. The results obtained with a scan speed of 20°C min^{-1} are given in *Table 2*. The absence of a glass transition in the blends with compositions under 40% (w/w) in P2VP is also noteworthy. The PMEI–P4VP blends do not show a glass transition before PMEI degradation at any composition. This could be attributed to the fact that the glass transitions in the blends are overlapped by the thermal degradation processes. As can be observed from *Figure 3*, at higher temperatures the blends show a wide degradation peak similar to that observed for the complexes. The peak temperature is higher, the higher is the poly(vinylpyridine) content in the blend. Furthermore, this temperature is lower than that detected in complexes for all blends studied.

The thermogravimetric curves for the homopolymers and two complexes are displayed in *Figure 4*. The PMEI thermogravimetric curve shows a first degradative step between 155 and 270°C and, overlapped with this, a new series of degradative reactions, which take place at high temperatures. The *FT*i.r. experiments performed at high temperature suggest that the first process can be attributed to the formation of cyclic and linear anhydrides, with loss of water and ethanol[14,16]. At high temperatures, decarboxylation processes, with loss of CO_2 and CO molecules, occur in conjunction with anhydride formation. In contrast, poly(vinylpyridine)s show a higher thermal stability.

When thermogravimetric experiments on PMEI–P2VP and PMEI–P4VP complexes are performed, the first degradative process observed takes place in the range ≈ 140–230°C (see *Figure 4*). This agrees with the results obtained by d.s.c. analyses, which suggest that PMEI presents a higher thermal stability than its complexes. Thermal behaviour is different above 230°C. PMEI–P4VP complexes exhibit a well defined second degradative process, which finalizes near 350°C. PMEI–P2VP complexes show a series of overlapped degradative steps till the end of the experiment.

PMEI–P2VP and PMEI-P4VP blends follow a general degradative behaviour similar to that observed in the homologous complexes. In *Figures 5a* and *5b* are shown some thermogravimetric curves for PMEI–P2VP and PMEI–P4VP blends respectively. The mass loss starts at lower temperature (≈ 120°C) than for the complexes. Blends involving P2VP show an onset of degradation independent of blend composition (*Figure 5a*). The onset of degradation temperature in PMEI–P4VP blends increases as P4VP proportion increases (see *Figure 5b*).

The experimental thermal degradation curves can be compared with those calculated from pure components assuming an additive behaviour. These curves are given in *Figures 4* and *5*. As can be seen from these figures, although the degradative processes involved in the blends seem to be similar to those of the pure components, they show remarkable differences in position and magnitude. Thus, PMEI–P2VP blends show an onset of degradation around 35°C lower than the theoretical one and 16°C for PMEI–P4VP blends. A second remarkable difference is observed in the degradative processes at higher temperatures. Considering the process corresponding to poly(vinylpyridine)s, degradation takes place for PMEI–P4VP blends 24°C before that for pure P4VP. This difference is 20°C in PMEI–P2VP blends. Finally, in both blends the yield of thermal degradation is notably higher than the theoretical one calculated assuming an additive behaviour.

Thus, poly(vinylpyridine)s seem to have a 'catalytic effect' in the decomposition of PMEI. This is not a surprising result taking into account that pyridine rings are well known catalysts for hydrolysis of esters, or decarboxylation of acids[17], typical processes in the

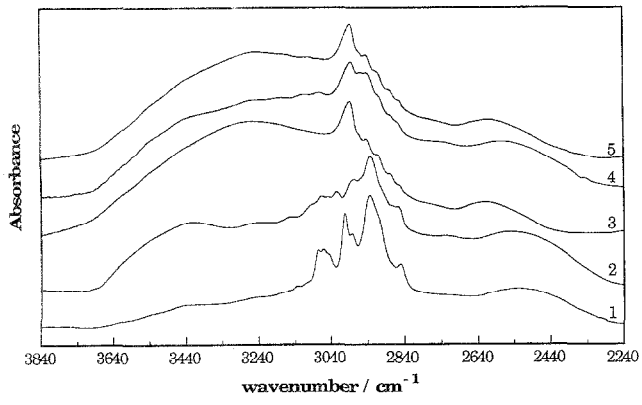

Figure 7 Scale-expanded infra-red spectra in the hydroxyl stretching region for: (1) PMEI–P2VP blend (P2VP weight fraction = 0.5); (2) PMEI–P4VP blend (P4VP weight fraction = 0.5); (3) PMEI; (4) PMEI–P2VP complex (P2VP feed weight fraction = 0.5); and (5) PMEI–P4VP complex (P4VP feed weight fraction = 0.5)

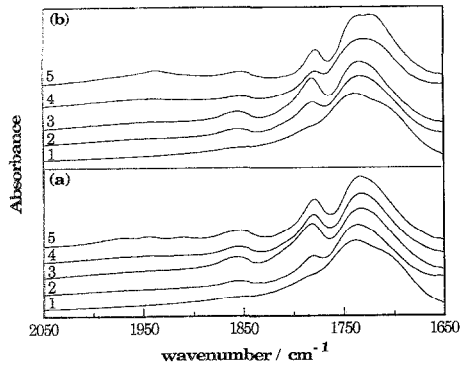

Figure 8 Scale-expanded infra-red spectra in the carbonyl stretching region. (a) (1) PMEI; (2) PMEI–P2VP complex (P2VP feed weight fraction = 0.2); (3), (4) and (5) PMEI–P2VP blends (P2VP weight fraction = 0.2, 0.5 and 0.8 respectively). (b) (1) PMEI; (2) PMEI–P4VP complex (P4VP feed weight fraction = 0.2); (3), (4) and (5) PMEI–P4VP blends (P4VP weight fraction = 0.2, 0.5 and 0.8 respectively)

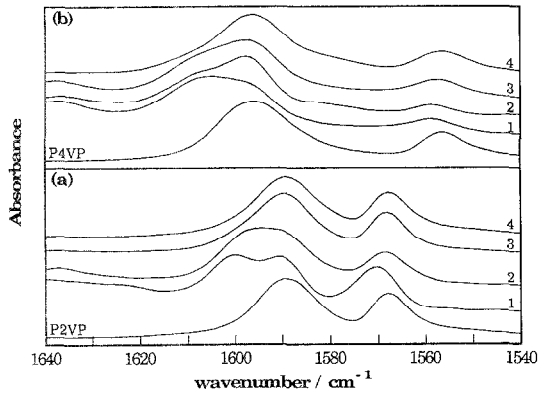

Figure 9 Scale-expanded infra-red spectra in the pyridine ring stretching region. (a) (1) PMEI–P2VP complex (P2VP feed weight fraction = 0.2); (2), (3) and (4) PMEI–P2VP blends (P2VP weight fraction = 0.2, 0.5 and 0.8 respectively). (b) (1) PMEI–P4VP complex (P4VP feed weight fraction = 0.2); (2), (3) and (4) PMEI–P4VP blends (P4VP weight fraction = 0.2, 0.5 and 0.8 respectively)

thermal degradation of poly(monoalkyl itaconates)[16]. The differences observed using the two poly(vinylpyridine) isomers could be explained by taking account of steric effects. If we consider the nitrogen atom in the pyridine ring as the main reactive point of poly(vinylpyridine)s, the nitrogen atom in P4VP could react more readily than that in P2VP. These reactions could occur either with PMEI or with poly(vinylpyridine) itself.

Infra-red analysis

The infra-red spectrum of PMEI shows the characteristics typical of an associated polyacid (see *Figure 6*). Thus, the hydroxyl stretching region exhibits a broad band centred at 3230 cm^{-1}. The contribution of non-bonded hydroxyl groups (around 3550 cm^{-1}) is not appreciable and the absence of a dominant contribution at around 3100 cm^{-1}, typical in other polyacids[18], indicates that dimerization is not the main type of self-association in PMEI. Finally, a satellite band is detected at 2620 cm^{-1}, which can be attributed to associated hydroxyl groups and is common in other carboxylic acids.

The carbonyl stretching region of poly(monoitaconates) is rather complicated[5,16]. Similarly to PMMI[5], five significant contributions can be distinguished at least: two minor contributions at high wavenumbers, 1850 and 1780 cm^{-1}, attributable to cyclic anhydrides formed during the polymerization process; two main contributions centred at 1737 and 1700 cm^{-1}, corresponding to the carbonyls in ester groups and acid groups, respectively; and finally, a weak band at 1645 cm^{-1}, attributable to residual diketone structures formed in the polymerization process.

The infra-red spectrum of poly(vinylpyridine)s has been described[5]. The most remarkable bands are the characteristic modes of the pyridine ring at 1590, 1050 and 993 cm^{-1} for P2VP and 1597, 1493 and 993 cm^{-1} for P4VP.

The spectral characteristics of polycomplexes and blends are quite similar. Both systems show evidence of hydrogen bonding among the components. In this connection, it should be noted that the hydroxyl and carbonyl stretching modes of PMEI and the ring modes of the pyridine group in polycomplexes and blends undergo significant changes with respect to the homopolymer precursors. *Figure 7* shows the hydroxyl stretching region. We wish to emphasize the presence of two satellite bands centred at ≈ 2560 and ≈ 1940 cm^{-1}; these bands are typical of strong hydrogen-bonded systems[5,6,19]. This last band (see *Figure 8*) becomes clearer, the higher the poly(vinylpyridine) ratio in the blend, and its intensity is higher in PMEI–P4VP blends than in PMEI–P2VP ones. Another interesting feature in this spectral region is an increment in the hydroxyl contributions at wavenumbers higher than those observed in pure PMEI. This fact can be associated with a partial conversion of PMEI–PMEI hydrogen bonding to PMEI–poly(vinylpyridine) interactions.

The carbonyl stretching region in complexes and blends also shows important differences with respect to that of PMEI (see *Figures 8a* and *8b*). This complicated zone exhibits a main band centred around 1735 cm^{-1} narrower than that in pure PMEI. This fact may be attributed to a change in the hydrogen-bonding distribution as a consequence of the PMEI–poly(vinylpyridine) interactions. In this connection, for PMEI–P4VP blends (*Figure 8b*) a double carbonyl band (1734 and 1723 cm^{-1})

is observed for P4VP ratios above 60%. The band at 1723 cm^{-1} is ascribed to carbonyl groups associated not with hydroxyl groups but with pyridine nitrogen atoms. It is interesting to note that the fraction of carboxylic groups bonded to pyridine nitrogen atoms is higher, the higher the P4VP ratio in the blend. On the other hand, the band at 1723 cm^{-1} is vague in PMEI–P2VP systems (*Figure 8a*). This is due to the smaller ability of P2VP for complexation. Finally, the carbonyl interaction redistribution leads to a better definition of the bands corresponding to cyclic anhydrides.

The pyridine ring modes associated with several systems are shown in *Figures 9a* and *9b*. This spectral region offers important information about the interactions established between PMEI and poly(vinylpyridine)s. A new band located around 1600 cm^{-1} is found for PMEI–P2VP complexes and blends. The same applies for PMEI–P4VP complexes prepared from pyridine or methanol solutions. These systems show a double band whose maxima are located at 1597 and 1608 cm^{-1}. These displacements of the pyridine ring modes towards higher wavenumbers are characteristic of hydrogen-bonded pyridine rings[5,11,20]. These bands can be used for determining quantitatively the fraction of pyridine groups not associated with carboxylic acid groups of PMEI. According to Lee *et al.*[6], the fraction of pyridine groups not associated with PMEI carboxylic acid groups can be calculated as:

$$f_F^N = \frac{A_{1590}}{A_{1590} + (\epsilon_{1600}/\epsilon_{1590})A_{1600}} \quad (1)$$

where A are the areas of the bands (absorbances) and ϵ the absorption coefficients.

The previous equation could be simplified assuming that the absorption coefficient ratio is unity. To verify this approach, the band located at 1570 cm^{-1} could be used as internal reference since it does not seem to be affected by the existence of PMEI–P2VP interactions. Should the absorption coefficients change, this would give variations of the fractional area corresponding to the 1570 cm^{-1} band. As can be seen in *Tables 3* and *4*, the fractional area of the 1570 cm^{-1} band, defined as $f_A = A_{1570}/(A_{1570} + A_{1590} + A_{1600})$, remains constant, which indicates that ϵ_{1600} and ϵ_{1590} can be considered to have the same value. Therefore, equation (1) can be simplified to:

$$f_F^N = \frac{A_{1590}}{A_{1590} + A_{1600}} \quad (2)$$

Similarly, a free pyridine group fraction could be defined for PMEI–P4VP blends, assuming that the absorption coefficient ratio of the two bands is unity:

$$f_F^N = \frac{A_{1597}}{A_{1597} + A_{1608}} \quad (3)$$

An evaluation of the free pyridine groups in the blends and complexes has been performed using equations (2) and (3). The results are summarized in *Tables 3*, *4*, *5* and *6*. It is interesting to note from these tables that the fraction of free pyridine groups increases as the poly(vinylpyridine) content increases in the blends. The PMEI–P2VP and PMEI–P4VP complexes exhibit a fraction of free pyridine around 0.25 and 0.30 respectively. For a 20% P2VP feed composition, we obtain a fraction of free pyridine groups of 0.5. This fact can be explained by the higher content in P2VP than the other complexes (see *Table 1*). Thus, as expected, hydrogen bonds are stronger in complexes than blends.

The infra-red spectra of blends and polycomplexes seem to show evidence of partial protonation of the pyridine groups. A careful inspection of these infra-red spectra allows one to detect the presence of a small band located around 1638 cm^{-1} in PMEI–P4VP complexes and in PMEI–P2VP and PMEI–P4VP blends. In the case of PMEI–P2VP complexes, a similar band is observed at 1628 cm^{-1}. This kind of band has been described previously in sulfonated polystyrene and poly(ethyl acrylate-*co*-4-vinylpyridine) ionic blends[21], being fairly common also in blends of low-molecular-weight compounds with pyridine[20]; in both cases, this band is attributed to the presence of protonated pyridine groups. In summary, the PMEI–poly(vinylpyridine) systems studied here show specific interactions of the

Table 3 Curve-fitting data from infra-red spectra of PMEI–P2VP complexes

P2VP feed weight fraction	ν_1 (cm^{-1})	A_{1570}	ν_2 (cm^{-1})	A_{1590}	ν_3 (cm^{-1})	A_{1600}	f_F^N	f_A
0.20	1570	64	1590	79	1600	82	0.49	0.28
0.40	1571	57	1591	28	1600	95	0.23	0.32
0.50	1571	67	1591	33	1600	104	0.24	0.32
0.60	1571	82	1591	38	1600	126	0.23	0.33
0.80	1571	28	1591	15	1600	44	0.25	0.32

Table 4 Curve-fitting data from infra-red spectra of PMEI–P2VP blends

P2VP weight fraction	ν_1 (cm^{-1})	A_{1570}	ν_2 (cm^{-1})	A_{1590}	ν_3 (cm^{-1})	A_{1600}	f_F^N	f_A
0.20	1569	47	1589	65	1598	70	0.48	0.26
0.40	1568	263	1589	500	1598	165	0.75	0.28
0.50	1568	357	1589	642	1598	165	0.79	0.30
0.60	1568	355	1589	637	1598	131	0.83	0.31
0.80	1568	419	1589	822	1598	66	0.92	0.32

Table 5 Curve-fitting data from infra-red spectra of PMEI–P4VP complexes

P4VP feed weight fraction	ν_1 (cm^{-1})	A_{1597}	ν_2 (cm^{-1})	A_{1608}	f_F^N
0.20	1597	44	1608	100	0.30
0.40	1597	59	1608	156	0.27
0.80	1597	28	1608	67	0.29

Table 6 Curve-fitting data from infra-red spectra of PMEI–P4VP blends

P4VP weight fraction	ν_1 (cm^{-1})	A_{1597}	ν_2 (cm^{-1})	A_{1608}	f_F^N
0.20	1598	103	1608	75	0.58
0.40	1597	143	1608	92	0.61
0.50	1597	218	1608	106	0.67
0.60	1596	413	1608	120	0.77
0.80	1597	912	1608	158	0.85

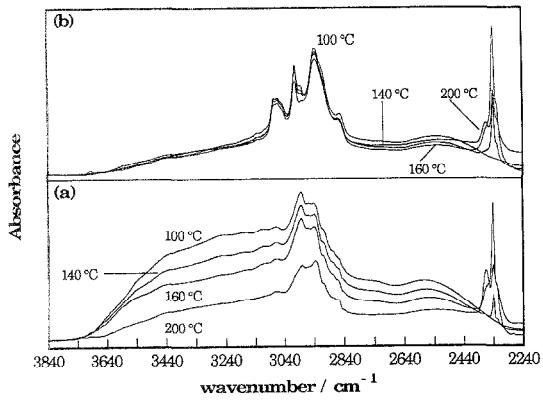

Figure 10 Hydroxyl stretching region for (a) PMEI–P2VP complex (P2VP feed weight = 0.5) and (b) PMEI–P2VP blend (P2VP weight fraction = 0.5) at several temperatures

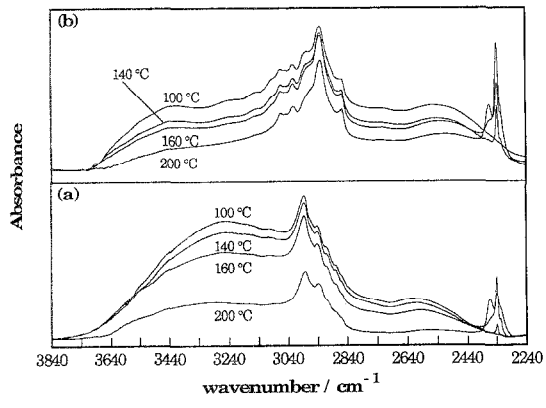

Figure 11 Hydroxyl stretching region for (a) PMEI–P4VP complex (P4VP feed weight fraction = 0.5) and (b) PMEI–P4VP blend (P4VP weight fraction = 0.5) at several temperatures

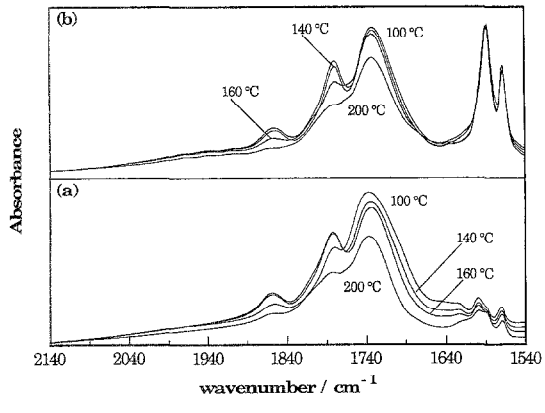

Figure 12 Carbonyl stretching region for (a) PMEI–P2VP complex (P2VP feed weight fraction = 0.5) and (b) PMEI–P2VP blend (P2VP weight fraction = 0.5) at several temperatures

hydrogen-bonding type, the intensity of such interactions being dependent on the system analysed. A partial protonation of the poly(vinylpyridine)s is also observed. Similar results have been reported by other investigators who employed poly(vinyl-pyridine)s as the proton acceptor polymer[4,6].

Analysis of the thermal behaviour has been completed by studying the infra-red spectra in the temperature range of 25–200°C. For all the samples studied, strong alterations are observed in different spectral regions related to hydrogen-bond breaking and to PMEI thermal

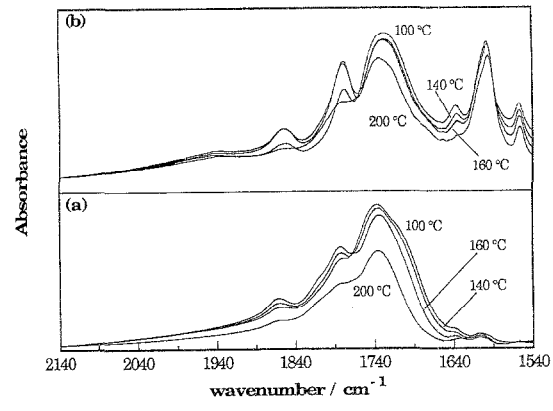

Figure 13 Carbonyl stretching region for (a) PMEI–P4VP complex (P4VP feed weight fraction = 0.5) and (b) PMEI–P4VP blend (P4VP weight fraction = 0.5) at several temperatures

degradation. The hydroxyl stretching region, represented in *Figures 10* and *11*, undergoes an evolution with temperature characterized by a progressive decrease in absorbance. As temperature increases, a higher proportion of non-associated hydroxyl groups (approximately 3540 cm^{-1}) is observed. In the same way, the satellite bands also present a downward tendency. These effects could be explained by the progressive loss of hydroxyl groups (in the form of ethanol and/or water) due to anhydride formation from PMEI with temperature.

Anhydride formation generates well known changes in the carbonyl stretching region. Thus, as can be seen from *Figures 12* and *13*, an increase of the intensity of the bands corresponding to cyclic anhydrides (1780 and 1850 cm^{-1}) is observed for temperatures above 120°C. Simultaneously a gradual reduction in the absorbance of other types of carbonyl stretching vibrations occurs. At temperatures above 160°C, the intensities of the carbonyl bands corresponding to cyclic anhydrides begin to decrease and bands associated with the formation of linear anhydride appear. This leads to the physical cross-linking of the samples, which makes them insoluble, as proved from solubility tests. The presence of bands corresponding to CO_2 (occluded in the KBr pellets) should also be noted here. This fact is relevant at temperatures higher than 160°C. Thus, at these temperatures, decarboxylation reactions take place in conjunction with anhydride formation. Both processes yield a decrease of the carbonyl vibration band intensity.

CONCLUSIONS

The results obtained in this work confirm that PMEI and poly(vinylpyridine)s form polymer–polymer complexes through hydrogen bonding when methanol is used as solvent. The stoichiometry of these polycomplexes relies on the starting feed composition; nevertheless, the results obtained seem to indicate a more favourable stoichiometry of 2 : 1 of monoethyl itaconate : vinylpyridine repeat units. The use of a solvent that could compete with the pyridine groups to establish hydrogen bonds with PMEI allows one to get blends of preset composition.

The thermal behaviour of polycomplexes and blends, up to 200°C, indicates the existence of different degradative processes related to PMEI. The degradative reactions start around 140°C with the formation of cyclic anhydrides. At higher temperatures, linear anhydride

formation becomes important, which leads to physical crosslinking of the material. Overlapped with these processes are decarboxylation reactions with loss of CO and CO_2.

The *FT*i.r. analyses clearly show evidence of the existence of hydrogen bonding between the PMEI and the poly(vinylpyridine)s, with partial pyridine group protonation. This technique allows one to make a quantitative evaluation of the grade of association in polycomplexes and blends. All the extracted data seem to indicate that, in the polycomplexes, effective physical crosslinking forming a three-dimensional structure is produced. The use of pyridine as solvent decreases the efficacy of the polymer–polymer interactions, allowing soluble blends to be obtained.

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