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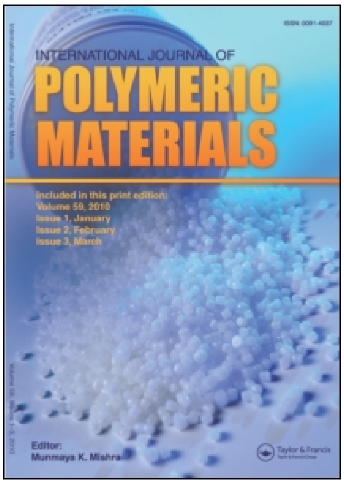

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Blends of Poly(vinylpyrrolidone)/Poly(monoitaconates). I Interpolymer Complex Formation

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Blends containing poly(vinylpyrrolidone) (PVP) of three different molecular weights and poly(monoitaconates) (PMI) with different side chain structures were prepared. Polymer blends of various compositions were analyzed by Differential Scanning Calorimetry (D.S.C.). The calorimetric study was performed on films prepared from methanol and dimethylformamide (DMF). One Tg value is observed for the majority of the samples over a wide range of composition, but in all cases a minimum in the Tg-composition diagram is observed which is attributed to an interpolymer complex formation. The analysis of these systems in solution by using turbidimetry and viscometry techniques for PMMI/PVP confirms the results obtained in the solid state.

KEY WORDS Blends, complexes, poly(vinylpyrrolidone), poly(monoitaconates).

INTRODUCTION

Polymer blends containing poly(monoitaconates) (PMI) are scarce.[1] Nevertheless, this kind of polymers seem to be very interesting from a compatibility point of view, because they should be capable of hydrogen bond formation, through the carboxylic group.[1] Therefore, it should be possible to obtain compatible polymer blends by blending PMI with acceptor polymers such as poly(vinylpyrrolidone) (PVP). In fact, polymer-polymer miscibility can be observed in systems with specific interactions such as hydrogen bonds and dipole-dipole interactions.[2–5] In these systems interpolymer complex formation in solution have been reported.[6–10] This type of complexes have attracted much attention.[4,5,11,12] Polycomplexes are stabilized through different kind of interactions but mainly by hydrogen bonds. It is interesting to remark that in this group of polymer complexes, the system poly(acrylic acid)/poly(ethylene oxide) has been broadly studied[6,7,13–18] due to the interest in preparing compatible polymer blends.

The aim of this work is the study in the solid state of blends containing

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poly(monoitaconates) (PMI) with different side chains and poly(vinylpyrrolidone) (PVP) of different molecular weights in order to analyze the compatibility of these polymers. The comparison of these results with those obtained in solution for mixtures of poly(monomethyl itaconate) (PMMI) with PVP will be performed. On the other hand, the effect of the side chain structure of poly(monoitaconates) and the solvent casting on the compatibility will be analyzed.

EXPERIMENTAL

Monomer and Polymers

Commercial samples of poly(vinylpyrrolidone) (PVP) of three different molecular weights i.e., Mw: 10,000, 24,000, and 40,000 from Aldrich and labeled as PVP^{10}, PVP^{24}, PVP^{40}, were used.

Monomethyl itaconate (4-methyl hydrogen-2-methylene succinate) (MMI), monoethyl itaconate (4-ethyl hydrogen-2-methylene succinate) (MEI) and mono(decyl itaconate) (4-decyl hydrogen-2-methylene succinate) were prepared by reaction of itaconic acid (2-methylene succinic acid) with the corresponding alcohols under fairly acidic conditions according to methods previously reported.[19] Monomers were purified by dissolution in methanol and precipitation with diethyl ether.

Monomers were polymerized at 345 K under N_2 in the presence of α,α'-azo-bis-isobutyronitrile (AIBN) (0.3% mol) as initiator.

Molecular weights of the polymers were calculated from intrinsic viscosity values by means of the following equations[20,21]: $[\eta] = 5.05 \times 10^4 M_w^{0.5}$, and $[\eta] = 4.8 \times 10^4 M_w^{0.52}$ in methanol for PMMI and PMEI respectively and $[\eta] = 1.12 \times 10^4 M_w^{0.65}$, for PMDI in THF. Fractions of narrow molecular weights ($M_w/M_n \approx 1.2$) were obtained by fractional precipitation using methanol-diethyl ether as solvent-precipitant pair.

Preparation of the Blends

PVP-PMI blends of different compositions were prepared by solution casting using methanol and/or dimethylformamide (DMF) and then evaporated at room temperature and vacuum dried at 30°C by 72 h. The polymer concentration in the solution was about 2% (w/w). Solvent evaporation was conducted at room temperature. The resulting films were dried in a vacuum oven at 35°C over 72 h. In some cases blends in solution were precipitated with diethyl ether under vigorous stirring.

For solution measurements, samples were prepared by mixing stock solutions of the corresponding polymers in the appropriate proportion and standing 24 h before measurements. For each series of experiments the concentration of PMI was maintained constant and the PVP concentration was varied in order to adjust the relation τ = [PVP]/[PMMI] to the required volume.

Measurements in Solution

Turbidimetry measurements were performed in a Shimadzu Spectronic 20 at 344 nm where no absorption due to the homopolymers were detected. Measurements were carried out in solutions of different concentration at different τ values, between 0 to 2.

Viscosity measurements were performed with a Desreux-Bischoff[22] capillar dilution viscometer. The capillary size chosen was such that kinetic energy corrections were negligible and the temperature controlled to $\pm 0.02°C$. The intrinsic viscosity $[\eta]$ results for different concentrations, τ, and pH were determined by means of the Solomon-Gotessman[23] equation.

Calorimetric 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 and a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Samples were weighted into the DSC aluminum pans. Dry nitrogen were used as purge gas and thermograms were measured in the range 300 to 500 K at a scan rate of 10 K min^{-1}. Regular calibration of the instrument was carried out using metal standards.

Before measuring the glass transition, all samples were first heated to the annealing temperature previously determined for the corresponding homopolymers. The glass transition was located as baseline shift on the thermograms and Tg was estimated from the point of intersection of the sloping portion of the curve resulting from the baseline shift. Each blend was scanned several times in the temperature range described above.

Annealing experiments were performed by heating the polymer samples to the selected annealing temperature and maintaining it at this temperature for 20 min. This period was found by experiment to be long enough to attain a distinct phase separation in these samples in the temperature range of interest but not long enough to produce degradation of the polymer.

RESULTS AND DISCUSSION

The DSC thermograms of the samples isolated from the solvents, containing initially differing amounts of PMI and PVP exhibit distinct single glass transitions temperatures (Tg) what should be indicative of one phase material.

Figure 1 shows the variation of Tg with composition for blends of PVP^{10}, PVP^{24}, and PVP^{40}, with poly(monomethyl itaconate) (PMMI) of Mw = 35,000. The plot corresponding to the Blends of PVP^{24}-PMMI obtained from dimethylformamide (DMF) is also included. As it can be seen one Tg value is obtained for different compositions. In the case of PVP^{10}-PMMI there is a monotonically variation of Tg as function of composition with a pronounced deviation from linearity. This behaviour is similar to that reported for compatible polymer blends.[24] Unfortunately it is not possible to obtain the Tg value for PMMI, because it cannot be clearly detected. Nevertheless, as the last point is at a composition near that of the homopolymer, it would be possible to obtain the Tg value by extrapolation to 100% composition. By this way it should be possible to analyze this Tg-composition

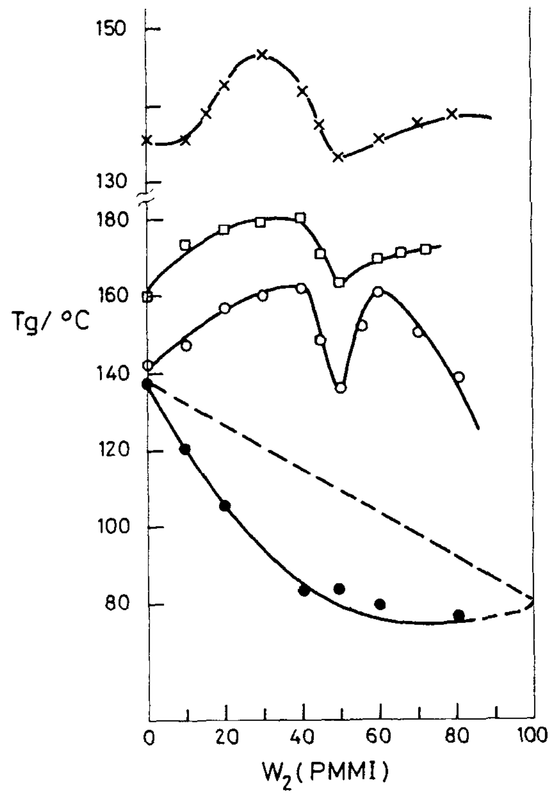

FIGURE 1 Variation of the glass transition temperature Tg with composition of PMMI (w_2) for blends of PMMI with PVP^{10} (●), PVP^{24} (○), PVP^{40}(□) obtained from methanol and for PVP^{24} (×) obtained from dimethylformamide.

diagram assuming compatibility between these polymers, by using the Gordon-Taylor[25] equation:

$$\mathrm{Tg} = \frac{w_1 \mathrm{Tg}_1 + k w_2 \mathrm{Tg}_2}{w_1 + k w_2} \tag{1}$$

where Tg_i are the glass transition temperatures of the corresponding homopolymers and k is a parameter dealing with the strength of the interaction. The k parameter of the Gordon-Taylor equation for the blend PVP^{10}-PMMI as shown in Figure 1 is 0.45 what would be indicative of compatibility with a strong interaction between polymers.

In Figure 1 we can also observe the variation of Tg with composition for blends containing PVP samples of higher molecular weight than in the former, i.e., PVP^{24}-PMMI and PVP^{40}-PMMI blends obtained by casting from methanol solutions. In all cases one Tg value intermediate between the Tg values of the individual components is obtained. But, the shape of these curves are very different from that containing PVP^{10}. A very interesting point is that these curves show a minimum in Tg at a composition about 50%. This behaviour is suggestive of a strong tendency towards a common composition (50%, $\tau = 1$) irrespective of the starting stoichiometry. Similar behaviour has been reported for other polymers,[8] and it has been interpreted as an interpolymer complex formation with a characteristic Tg value. The same behaviour is observed when blends are prepared from dimethylformamide.

In order to know in a more detailed way if this particular behaviour is general for PVP-PMI blends we have studied blends containing another poly(monoitaconates). Therefore, we have analyzed the effect of the side chain structure of two poly(itaconates) on the polymer complex formation with PVP.

Figure 2 shows the Tg-composition diagrams for blends containing poly(monoethyl itaconate) (PMEI) and poly(monodecyl itaconate) (PMDI) i.e. PVP^{24}-PMEI, PVP^{40}-PMEI from methanol solutions and PVP^{24}-PMDI from *n*-butanol. As can be seen in these curves a minimum in the Tg-composition plot is obtained which is more or less pronounced, depending on the molecular weight and/or on the polymer structure. Nevertheless, in the case of PVP^{40}-PMEI and PVP^{24}-PMDI there is a steep fall in Tg as the PMI composition increases and the minimum is reached about 45–50%. Polymer complexes can be considered as one-phase blends but

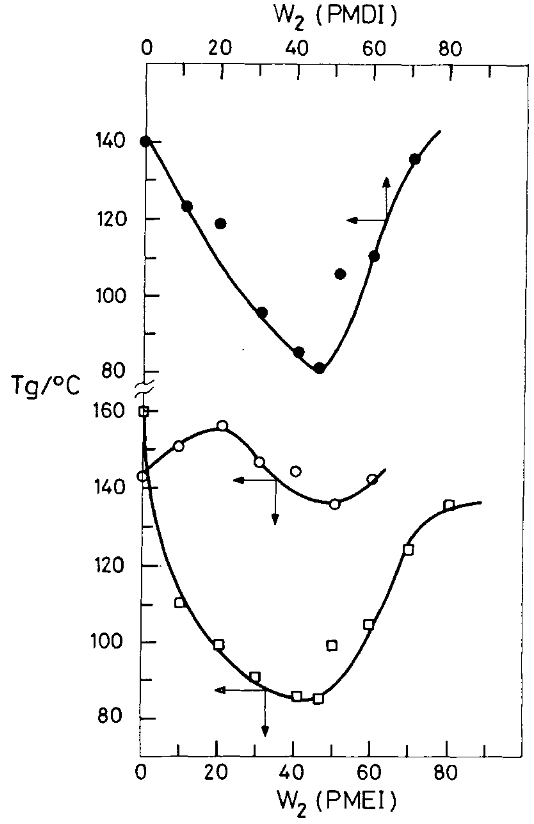

FIGURE 2 Variation of the glass transition temperature Tg with composition (w_2) for blends of PMEI with, PVP^{24} (○), PVP^{40}(□), and blends of PVP^{24} and PMDI (●).

with a single and limited composition, normally equimolar.[8] However, in the case of these systems we can see that all the compositions show only one Tg value that should be indicative of one phase system.

These results seems to indicate that poly(vinylpyrrolidone) and poly(mono itaconates) should give rise to polycomplex by hydrogen bonds, where the carboxylic group of poly(monoitaconates) should play an important role. It is very interesting to note that this kind of association is observed in the solid state, which would indicate the formation of a compatible polymer blend by complexation. Similar results have been reported by Bimendina[26] for PMMI and PVP in aqueous solutions.

In order to investigate the interpolymer complex formation in solution and to compare with the results obtained in the solid state, we have prepared different blends of PMMI-PVP[24] from aqueous and organic solutions, following the variation of the intrinsic viscosity $[\eta]$ and the transmittance for different solutions. Depending on the concentration and pH of the solution it is possible to see a steep fall of the transmittance for solutions of different τ values (being $\tau = [\mathrm{PVP}]/[\mathrm{PMMI}]$) as it can be seen in Figure 3 for three concentrations. But, irrespective of the concentrations or pH, when the change in transmittance take place, $\tau = 1$. For higher pH values there is a linear variation of the transmittance with τ that can be interpreted as no polymer complex formation. These results are very similar to those reported by Bimendina et al.[26] but using different experimental techniques.

On the other hand Figure 4(a) shows the variation of the transmittance with pH for samples with $\tau = 1$ at the three concentrations studied. As can be seen there is an abrupt fall of the transmittance to values lower than 10%. On the contrary at $c = 0.1$ gdl^{-1} and pH $= 3$ the behaviour is rather different in the sense that

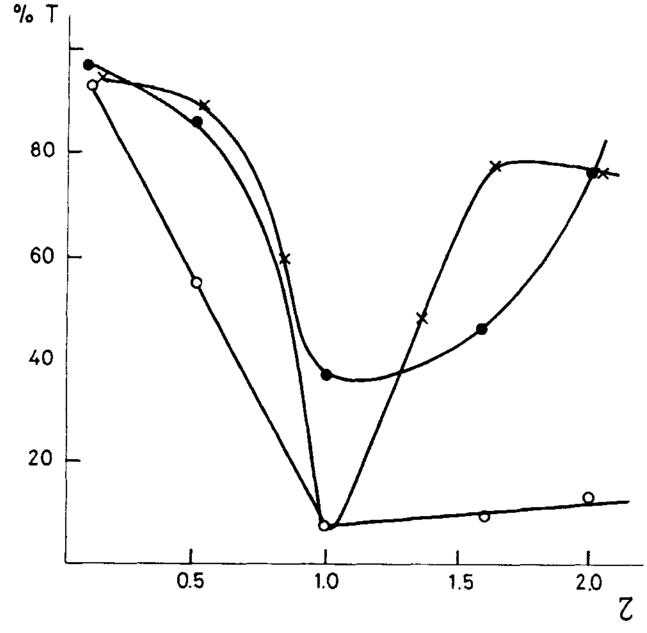

FIGURE 3 Variation of the transmittance with τ for blends of PMMI/PVP at three concentrations C and pH: 0.10 gdl^{-1}, pH $= 3.0$ (●); 0.15 gdl^{-1}, pH $= 3.0$ (○), and 0.30 gdl^{-1}, pH $= 4.0$ (×).

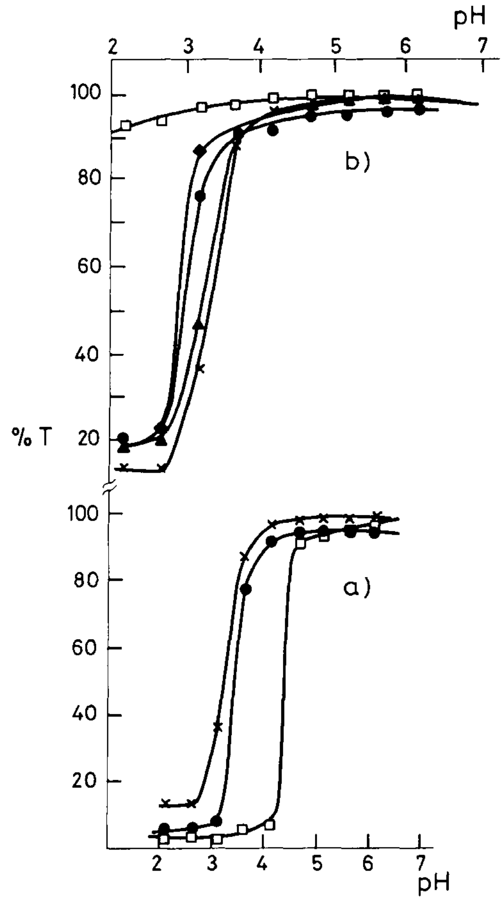

FIGURE 4 a): Variation of the transmittance with pH at three different initial concentrations (Ci) and τ = 1 (×) 0.10 gdl^{-1}; (●) 0.15 gdl^{-1} ( ) 0.30 gdl^{-1}. b): Variation of the transmittance with pH at different τ values: (●) τ = 2; (△) τ = 1.6; (×) τ = 1.0; (♦) τ = 0.5; (l) τ = 0.1.

transmittance remain about 40%. The effect of the initial concentration of the homopolymers seems to have influence in the critical conditions for the formation and precipitation of the polycomplexes. Figure 4(b) show the variation of the transmittance with pH at different τ values at 0.1 gdl^{-1}. As can be seen the lower value of transmittance where the maximum polycomplex formation is reached correspond for τ = 1. No polycomplex formation is observed for τ = 0.1 and pH values higher than 4 for the initial concentrations studied. For systems in which polycomplex formation take place, it is possible to observe precipitation of the polycomplex at a given critic pH (pH$_c$). This pH$_c$ has been reported for several systems such as poly(methyl methacrylate), poly(styrene-co-maleic anhydride) and poly(acrylic acid) with poly(ethylene oxide) and it has been reported that pH$_c$ increases with increasing the dissociation constant of polyacid.[27] The differences found in pH$_c$ values observed in the systems studied has been attributed to differences in the polymeric concentration.[27] In order to clarify this behaviour in the mixture PVP-PMMI we have analyzed the influence of the initial homopolymers concentration on pH_c. For this purpose we have taken as criterium, the transmittance of 50% for different initial concentrations of PVP and PMMI solutions.

Figure 5(a) shows the variation of the initial concentration Ci of the polymeric solutions and pH_c as defined above. According to the straight line observed we obtain the relationship $C_i = -04766 + 0.1808\ pH_c$. These results show the significant importance of the initial concentration on pH_c that is very important when blends of this kind of polymers are prepared. Similar results have been reported by Ikawa et al.[27] in which they found differences in pH_c for systems such as PEO/PMMA and PEO/PAA that was attributed to differences in the initial concentration. Therefore, it is understandable to obtain differences in the thermal behaviour of these polymer blends when they are prepared as casting from different solvents as it was discussed above (see Figure 1). In fact, the solvent effect found in the solid state when blends are prepared for methanol or dimethylformamide can be attributed to specific solvent effect on the polymer complex formation that is in some respects similar to that found in aqueous solutions at different initial concentration and then with different pH_c.

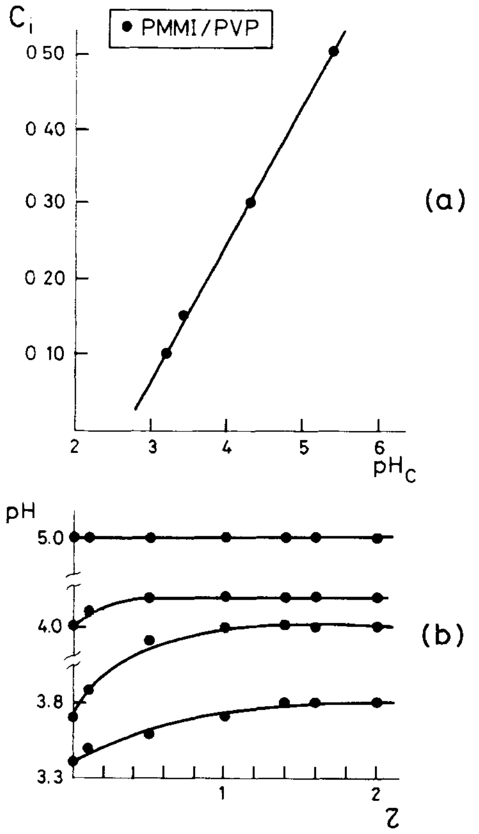

FIGURE 5 a) Variation of the initial concentration (Ci) of the polymeric solutions against critical pH for τ = 1. b) Variation of the pH with τ at different initial pH values.

In a previous paper we have reported the polyelectrolite behaviour of PMMI in aqueous solution[20] and depending on pH its intrinsic viscosity [η] change suddenly. The pH-viscosity data of Figure 6(a) and 6(b), shows that polycomplex take place at equimolar compositions of PVP and PMMI. On the other hand in Figure 5(b) we can observe the variation of pH with τ at different initial pH values reaching a particular value where no polycomplex formation is observed. According to these results it is possible to assume polycomplex formation as a compact structure with a small hydrodynamic volume, taking into account the found [η] value. As pH increases, that is to say as α_N, the degree of neutralization increases, the hydrodynamic volume is higher due to the expansion of the macromolecular coil by electrostatic interactions. Polycomplex formation gives rise to hipercoiled or compact structures with hydrodynamic volumes very reduced as it can be seen in the plots of Figure 6(a) and 6(b). Figure 6(c) shows the dependence of intrinsic viscosity with the degree of ionization of the complex. As can be seen there is a steep increase of the viscosity that can be attributed to the destruction of the complex which could exist only at certain values α_N.

If we pay attention on Figure 6(c) we can observe the influence of the degree of neutralization on the hydrodynamic volume of the complex. In fact, three zones can be distinguished; Zone I at low pH values where a compact structure of the complex is formed and precipitation takes place, zone II at pH values between 3.4–5.0 where a coiled structure is formed and no precipitation is observed, and zone III at high pH values where the carboxylic groups are neutralized and there is an expansion of the chain due to electrostatic repulsions giving rise to a less compact structure with a higher hydrodynamic volume. These results are in good

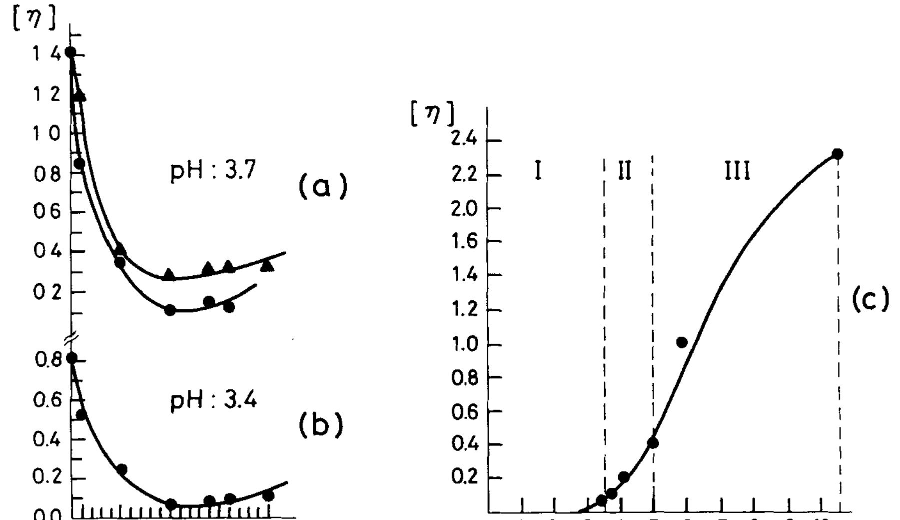

FIGURE 6 a) Variation of the intrinsic viscosity [η] with τ at pH 3.4 for two fractions of PVP. b) Variation of the intrinsic viscosity [η] with τ at pH 3.7 for one fraction of PVP. c) Variation of the intrinsic viscosity [η] with the degree of neutralization α_N of the polycomplex PVP/PMMI.

agreement with those reported by Ohno et al.[28] for the mixture PVP/PAA where they found a decreasing of intrinsic viscosity [η] when the polycomplex is formed in solution.

As it was mentioned above the formation of complexes structures between PVP and PMMI can be attributed to hydrogen bonds but hydrophobic interactions should play an important role in the stabilization of the compact structures in water.[19,29,30]

All the results presented in this work seem to indicate that poly(vinylpyrrolidone) and poly(monoitaconates) form policomplexes that can be detected in solution by different experimental techniques and in solid state by differential scanning calorimetry measurements where the presence of this kind of structures is manifested by a minimum in the Tg-composition diagrams. According to these results it is interesting to remark that polycomplex formation should be a very interesting way to obtain compatible polymer blends with properties intermediate to those of the corresponding homopolymers. New investigations considering different side chain structures of poly(monoitaconates) and poly(diitaconates) with polybases and the quantification of the forces involved in the interpolymer complexes are in progress.

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