Study of polymer blends based on poly(vinylpyridines) and acidic polymers

Malcolm B. Huglin and Jose M. Rego
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

(*Received 31 July 1989; revised 17 October 1989; accepted 23 October 1989*)

Binary blends of the basic polymers, poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP), with poly(2-acrylamido-2-methylpropanesulphonic acid) (PAMPS), which is strongly acidic, and poly[*N*-(3-sulphopropyl)-*N*-methacroyloxyethyl-*N*,*N*-dimethylammonium betaine] (PSPE), which is zwitterionic, have been prepared by mixing solutions of the separate components. The products were examined by infra-red spectroscopy and thermal analysis, which showed that no interactions occur in the blends PSPE/poly(vinylpyridines), whereas for the blends PAMPS/poly(vinylpyridines) the interactions were so strongly as to yield an insoluble polyelectrolyte complex. The influence of the position of the nitrogen atom in the pyridine ring was elucidated by determining the intrinsic acid dissociation constant of P2VP and P4VP by potentiometric titration against the monomer AMPS. Parallel measurements were also made on the viscometric behaviour during the incremental addition of AMPS to the basic polymers. From these results it can be concluded that the precipitation observed in the systems PAMPS/poly(vinylpyridines) is due to the formation of an effective crosslinking, which prevents chain expansion and subsequent reorientation of the chains in order to minimize the strong electrostatic repulsions between charged pyridine groups.

(Keywords: poly(2-vinylpyridine); poly(4-vinylpyridine); poly(2-acrylamido-2-methylpropanesulphonic acid); poly[*N*-(3-sulphopropyl)-*N*-methacroyloxyethyl-*N*,*N*-dimethylammonium betaine]; blends; complex formation; infra-red spectroscopy; thermal analysis; pH titration; viscometry; chain expansion; electrostatic repulsive interaction)

INTRODUCTION

Polymer blends have assumed increasing practical importance over the last 20 years. It is established that, of the features that influence miscibility between polymers, the most essential is the strength of interactions at a molecular level[1–3]. Among these, interactions of the acid–base type afford great flexibility in view of the range of strengths of such possible groupings that can be included into polymer chains. In the present study, we have selected as components of blends poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP), both of which are fairly weak bases, poly(2-acrylamido-2-methylpropanesulphonic acid) (PAMPS), which is strongly acidic, and poly[*N*-(3-sulphopropyl)-*N*-methacroyloxyethyl-*N*,*N*-dimethylammonium betaine] (PSPE), whch is zwitterionic. The formulae of these are given in *Figure 1*.

Other workers have reported that, when solutions of P2VP are mixed with solutions of weak acids such as poly(vinylphenol)[4] and ethylene-*co*-methacrylic acid[5] of certain compositions, a precipitate is produced. Blends involving bases other than P2VP have also been investigated[6–8]. Precipitation in such systems is generally attributed to the strong electrostatic attraction between oppositely charged macromolecules, yielding insoluble species, which are termed 'polyelectrolyte complexes'. If the electrostatic field of the polymers is suppressed by the addition of salts, the precipitate can frequently be dissolved or its formation prevented[9].

Commercial P4VP[10] has wide application not only for adsorption and recovery of soluble metallic species but also as a polymer reagent and catalyst support. Many of the diverse applications of PAMPS are based on the ability of the crosslinked polymer to produce a hydrogel of exceptionally high water content[11]. This capacity is due to the presence of the sulphonic acid group, which

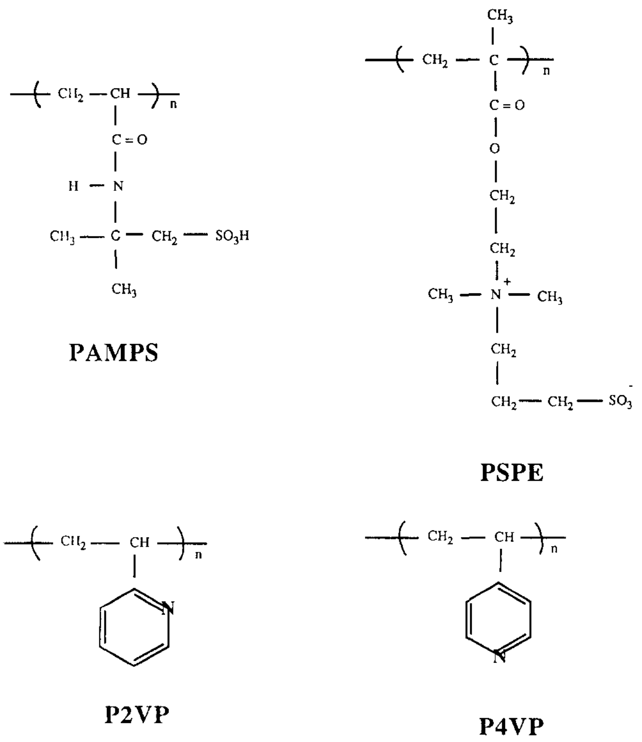

Figure 1 Molecular formulae of the components of the blends

0032-3861/90/071269-08

is fully ionized in water. This gives rise to strong ionic repulsions and, consequently, large chain expansion.

From the rather sparse existing information of PSPE, it emerges that this polymer is unusual in its antipolyelectrolyte behaviour, viz. higher viscosity and lower cloud-point temperatures in aqueous salt than in pure water[12]. Although (see *Figure 1*) there is some apparent structural similarity between this polymer and PAMPS, steric and acidic strength features seem likely to give rise to different behaviours in the corresponding blends with P2VP and P4VP.

In this paper, it is our intention to investigate the feasibility of polymer blend formation, utilizing various combinations of these potentially interactive polymers and, where appropriate, to characterize the polyelectrolyte complex formed.

EXPERIMENTAL

Materials

An aqueous solution of AMPS (Sigma Chemical Co.) and ammonium persulphate was outgassed with gaseous nitrogen for 1 h prior to polymerization at 323 K for 30 min. The initial concentrations of monomer and initiator were 0.406 mol dm^{-3} and 1×10^{-3} mol dm^{-3}, respectively. Unreacted monomer was removed by dialysis with deionized water for 3 days, and PAMPS was obtained as a white powder by freeze-drying and final drying in a vacuum oven at 314 K for 24 h. The yield was 40%. The molar mass of 5×10^5 g mol^{-1} was determined from the limiting viscosity number (*LVN*) measured in 5 M aqueous NaCl at 298 K in conjunction with the Mark–Houwink–Sakurada (MHS) constants[13].

The monomer SPE was kindly provided by Rasching Co. The polymerization was conducted in aqueous solution for 450 min at 333 K after intensive outgassing with gaseous nitrogen. The initial concentration of monomer was 0.556 mol dm^{-3} and that of the initiator (ammonium persulphate) was 4×10^{-3} mol dm^{-3}. A precipitate of PSPE was observed during the polymerization, this being in accordance with the previously mentioned cloud-point behaviour in water. The reaction solution was poured into a large excess of methanol, which is a good solvent for the monomer, this giving rise to the precipitation of the polymer, which was washed with methanol and dried in a vacuum oven at 313 K for 2 days.

The monomer 2VP (Aldrich Chemical Co.) was vacuum distilled twice before use (b.p. 301 K at 4 mmHg pressure) in the presence of cuprous chloride as inhibitor. The polymerization was conducted in bulk at 333 K for 180 min with 4,4′-azobis(cyanopentanoic acid) (1×10^{-3} mol dm^{-3}) as initiator, after degassing the reactive mixture for 1 h with gaseous nitrogen. The P2VP was isolated by precipitation in a large excess of petroleum ether (Sigma Chemical Co.), washed in this precipitant and dried to constant weight in a vacuum oven at 313 K. The conversion was low (2%) and the molar mass was determined to be 1.6×10^5 g mol^{-1} from the measured *LVN* in methanol at 298 K in conjunction with published MHS constants[14]. This sample will be denoted hereafter as P2VP-1. Samples of P2VP and P4VP, each of quoted molar mass of 0.4×10^5 g mol^{-1}, were also purchased from Polyscience Ltd. This P2VP from Polyscience will be denoted P2VP-2.

Preparation of blends

One of the few liquids capable of dissolving both PSPE and the poly(vinylpyridines) was found to be 2,2,2-trifluoroethanol (TFE). Separate solutions of PSPE, P2VP and P4VP, each 50 g dm^{-3}, were made up in TFE. For each of the systems PSPE/P2VP and PSPE/P4VP mixtures were then made in which the mole fraction of SPE units X_{SPE} was 0.20, 0.36, 0.47, 0.60 and 0.77. Both before and after the mixing, the solutions remained clear. For differential scanning calorimetry (d.s.c.) measurements, samples of solid blends were obtained by evaporation of solvent at 333 K; and for infra-red measurements, films were cast by solvent evaporation on KBr pellets.

With regard to blends of PAMPS with poly(vinylpyridines), selection of solvent media was dictated by the solubility of the former in water (but not in ethanol) and the solubility of the latter in ethanol (but not in water). It was found possible to maintain solubility of the separate parent homopolymers in ethanol/water (70/30 (v/v)) mixtures. Concentrations of 0.1 mol-segment dm^{-3} were used. For each of the systems PAMPS/P2VP and PAMPS/P4VP, blends were made by mixing, the mole fraction of AMPS units X_{AMPS} being 0.07, 0.22, 0.40, 0.60 and 0.85. The individual solutions were clear but, on mixing, white precipitates appeared immediately. These precipitates were isolated by centrifugation and then washed with aqueous ethanol prior to drying to constant weight in a vacuum oven at 313 K. For d.s.c. measurements, these samples were used directly; and for i.r. measurements, discs containing 2 wt% blend in KBr were prepared by compression.

Characterization

Fourier-transform infra-red spectroscopy. The infra-red spectra of homopolymers and blends were recorded on a Perkin–Elmer 1710 FTIR spectrophotometer. A minimum of 50 scans at a resolution of 2 cm^{-1} were averaged.

Differential scanning calorimetry. D.s.c. measurements were made with a Mettler TA-3000 instrument, which was previously calibrated with indium. The glass transition temperatures T_g were determined using a heating rate of 10 K min^{-1} and the middle point criterion. In order to avoid differences in thermal history, all the samples were subjected to the same thermal treatment, i.e. 10 min at 423 K.

pH titrations. pH titrations of P2VP in ethanol/water (70/30 (v/v)) and also of P4VP in the same solvent were performed at 293 K by means of a Corning Ion Analyzer model 150 using 1 mol dm^{-3} AMPS in the same solvent as titrant. The initial concentrations of the poly(vinylpyridines) were 2 g dm^{-3}. Using the same titrant, a corresponding blank titration was made against solvent alone in order to determine the degree of protonation (see below).

Solution viscosity. Using an Ubbelohde suspended-level dilution viscometer at 293 K, specific viscosities η_{sp} were measured after small incremental addition of AMPS solutions (1 mol dm^{-3}) to solutions of P2VP and P4VP, the initial concentration of these solutions being 4.23 g dm^{-3} and the solvent ethanol/water (70/30 (v/v)).

RESULTS AND DISCUSSION

Blends of PSPE/P2VP and PSPE/P4VP

Studies on PSPE have shown that the strong associations within PSPE hinder chain expansion and solubility in water. It is only when competition for the associating groups occurs by introduction of strongly associated salts that this self-association is broken and solution takes place[12]. *A priori*, it was useful to consider if the P2VP and P4VP could participate in an intermolecular process whereby the strong associations in PSPE are replaced by different interactions conducive to blend formation.

Figure 2 shows the spectra of PSPE, P2VP and P4VP. The main spectral features to be considered in order to interpret the behaviour of the blends are the deformation modes of the pyridine rings at 1570 and 1591 $\mathrm{cm^{-1}}$ for P2VP and at 1600 and 1557 $\mathrm{cm^{-1}}$ for P4VP. In principle, the deformation mode of the CH_3 attached to the nitrogen atom in PSPE, as well as the vibrations corresponding to the sulphonate group, could be of some usefulness. However, with regard to the former, its position (around 1430 $\mathrm{cm^{-1}}$), which sometimes renders it totally indistinguishable from the main CH deformation vibration, and its strength (very weak) diminish its usefulness. The sulphonate group vibrations are also of very little help due to the uncertainty of their position (several 'ranges' have been reported: 1150–1260, 1010–1080, 600–700 and 1170–1182 $\mathrm{cm^{-1}}$)[15].

The absorptions found in the region 3200–3500 $\mathrm{cm^{-1}}$ and at 1650 $\mathrm{cm^{-1}}$ in PSPE must be related to the presence of a volatile component, which, despite the drying of the polymer, is presumably residual solvent from the polymerization of PSPE (water) and/or precipitant (methanol). This has been proved by calorimetry, since the weights of the sample pans decreased by as much as 10% of the initial weight after thermal pretreatment.

Spectra of the blends PSPE/P2VP and PSPE/P4VP were obtained for different compositions. For each of

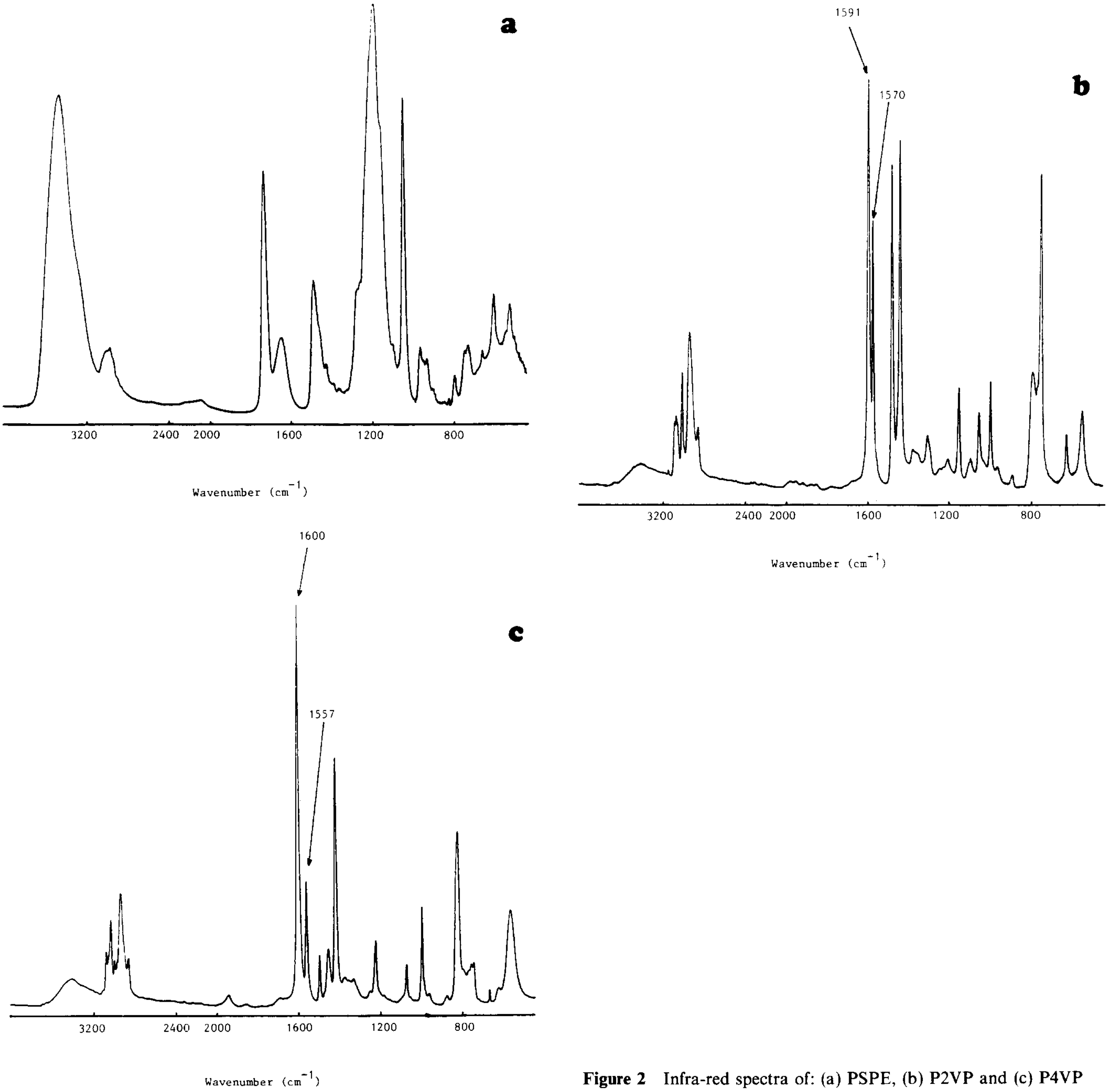

Figure 2 Infra-red spectra of: (a) PSPE, (b) P2VP and (c) P4VP

these two systems, changing composition affected the intensity but not the location of the bands. *Figure 3* shows the spectra of each of these types of blend for one composition only, viz. $X_{SPE}=0.20$. It is apparent that in both cases and regardless of the position of the nitrogen atom in the pyridine ring, there is no interaction between both polymers since no changes in the pyridine ring vibrations are detected.

The values of 373 and 423 K, which were obtained for the glass transition T_g of P2VP and P4VP, respectively, are in close agreement with those reported elsewhere[16]. The thermal behaviour of PSPE is, however, more complicated, as can be appreciated in *Figure 4*. Whilst the PSPE sample obtained by pouring the aqueous dispersion after polymerization into methanol displays only a broad glass transition at 428 K, the sample obtained by allowing the solvent TFE to evaporate shows a glass transition at 373 K and a broad melting point at 478 K. Despite some irreproducibility of results, the following general features are noted:

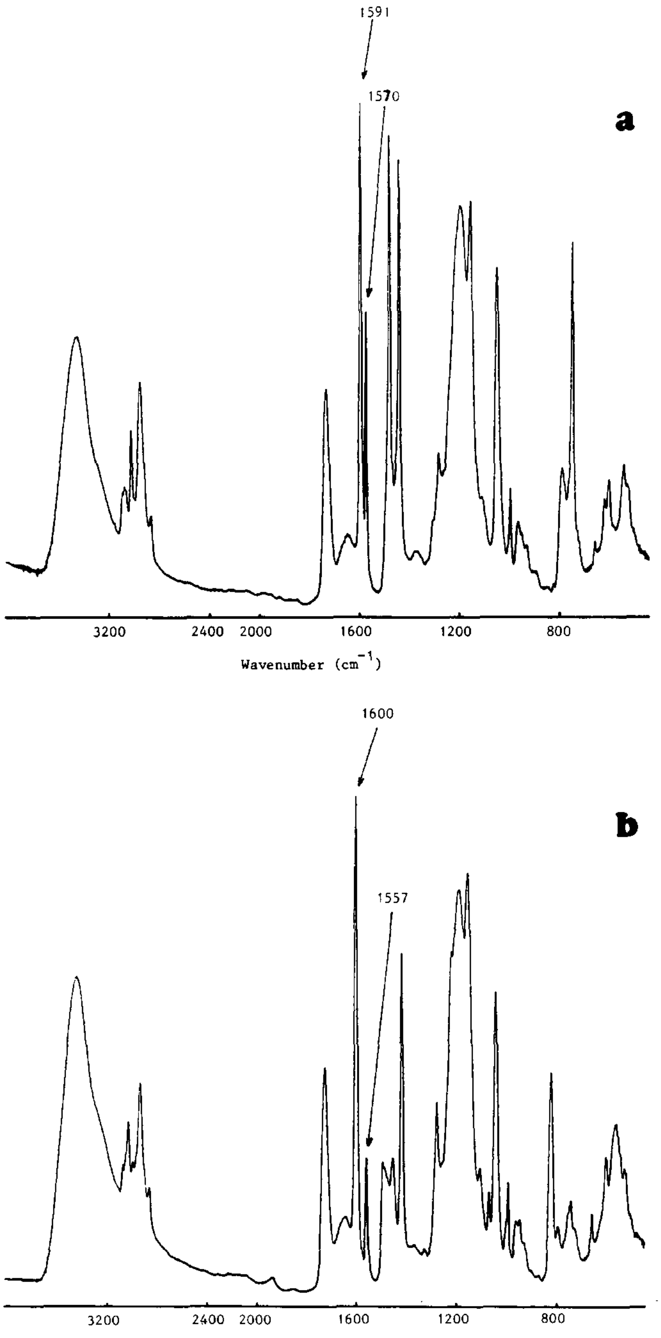

Figure 3 Infra-red spectra of the blends: (a) PSPE/P2VP and (b) PSPE/P4VP ($X_{SPE}=0.20$)

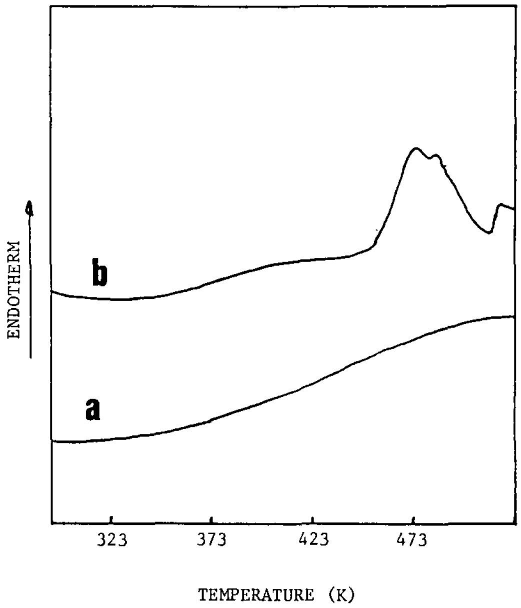

Figure 4 Thermograms of PSPE: (a) sample precipitated in methanol and (b) sample cast from 2,2,2-trifluoroethanol

PSPE/P2VP. Because the homopolymers have the same T_g (373 K), no useful information can be gained from the fact that one T_g at this same temperature was obtained experimentally for the blends.

PSPE/P4VP. (i) The T_g values of the homopolymers differ by ~50 K. (ii) Only one T_g is obtained between 373 and 423 K, without any clear correlation with composition. (iii) It should be realized that the miscibility that is indicated may be an apparent one because of the broadness of the T_g of PSPE and the possibility that any actual T_g of P4VP in the blend may be assimilated into the crystalline melting peak of the PSPE component.

Blends of PAMPS/P2VP and PAMPS/P4VP

PAMPS is a self-associated polymer. This assertion is supported by spectroscopic behaviour. The infra-red spectrum of PAMPS (*Figure 5a*) reflects the existence of a very strong intermolecular interaction, as can be concluded from the broad band at 3000 cm^{-1} and the satellite band at 2240 cm^{-1}. With regard to the band at 3000 cm^{-1}, it should be noted that the peaks due to CH stretching appear in the region 2900–3000 cm^{-1} and are partially displaced in intensity due to the band at 3000 cm^{-1} arising from hydrogen-bond formation between the proton in the sulphonic acid and the electron-donating nitrogen in the amide group (*Figure 5b*). Similar behaviour in blends of P2VP and poly(vinylphenol) has been noted by Coleman *et al.*[4]. The peak at 2240 cm^{-1} is often assigned to overtones and combination frequencies enhanced by Fermi resonance or anharmonic coupling of the ν_s (A–H stretching) and σ_s (H–B stretching) modes (A denotes acid and B base)[17]. Thermal analysis does not provide such strong corroborative evidence. The d.s.c. thermogram (*Figure 5c*) shows a broad glass transition in the region of 343–353 K and also three melting peaks, beyond which degradation

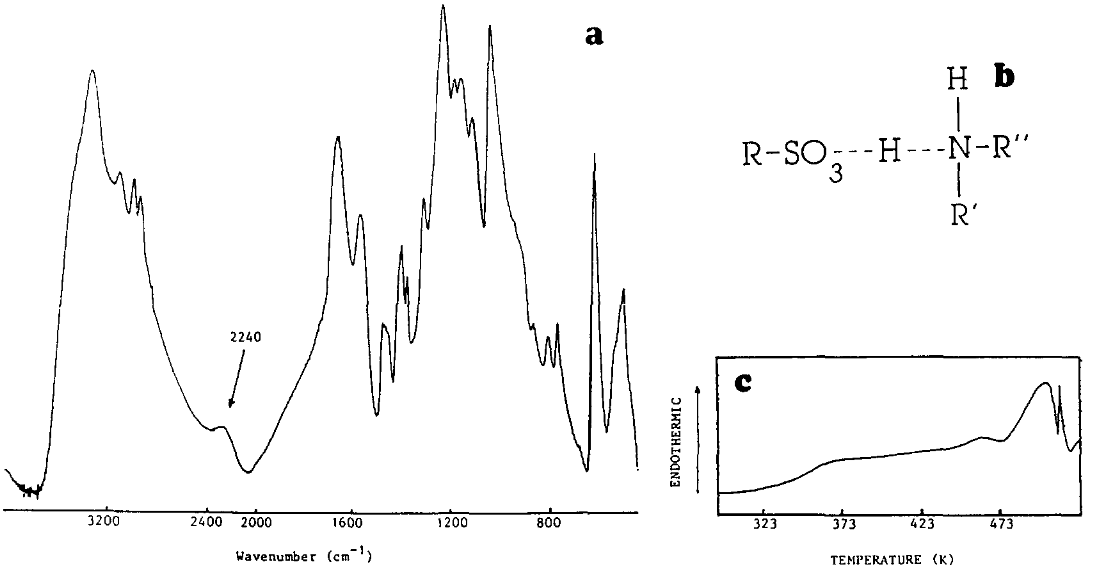

Figure 5 (a) Infra-red spectrum of PAMPS; (b) PAMPS self-associating mechanism; and (c) PAMPS thermal behaviour

occurs. It is not known if PAMPS is a crystalline polymer. As the synthesis used here was not one that would lead to stereospecific polymers, the existence of a melting peak must be indicative of disruption of order, such as the intermolecular interaction referred to previously. Moreover, the presence of more than one peak suggests that this structured form occurs at more than one level. In this connection, further evidence is discussed in the next section. We are, therefore, dealing with systems where the association between the two polymers first requires the dissociation of one of them (PAMPS), the poly(vinylpyridines) not being self-associated.

Figure 6 shows the spectra of the blends PAMPS/P2VP and PAMPS/P4VP (both poly(vinylpyridines) from Polyscience). For the sake of clarity, only the mole fractions of AMPS units ($X_{AMPS}=0.6$ for PAMPS/P2VP and 0.4 for PAMPS/P4VP) are shown, due to the fact that the spectra fit a general profile regardless of composition, the only difference being the decreasing presence of the characteristic pyridine ring vibrations, which have been amplified within the same figure. No differences due to molecular weight were found, this having been tested by using also the P2VP synthesized by us. The main spectral features of the blends are as follows:

(1) The appearance of a very broad band at approximately 2700 cm^{-1} for both systems, PAMPS/P2VP and PAMPS/P4VP, which is due to strong hydrogen bonding.

(2) The appearance of satellite bands at 2120 cm^{-1} for the system PAMPS/P2VP and 2140 cm^{-1} for the system PAMPS/P4VP. These are also due to hydrogen bonding arising from overtones and combination frequencies.

(3) The shifting of the NH deformation vibration (amide type), found at 1548 cm^{-1} in PAMPS, towards higher wavenumbers (1558 cm^{-1}) in the blends.

(4) The presence of the pyridine ring vibration modes at 1600 and 1557 cm^{-1} for P4VP and 1591 and 1570 cm^{-1} for P2VP and the disappearance of these bands with increasing content of PAMPS.

The first two points strongly suggest the existence of intermolecular association between the two constituent polymers in both systems. This interaction is, moreover, stronger than that found for the self-association of PAMPS itself (see *Figure 5*). The third point confirms this self-association in PAMPS since, once the sulphonic acid proton is taken by the pyridine group, the amide nitrogen in PAMPS is no longer donating its electrons to the proton and this brings about an increase of its resonance frequency. The fourth point, on the other hand, represents a behaviour that needs further comment, as it refers to the stoichiometry of the reaction. When we add the acid to the base, a compact, insoluble cluster appears (as was mentioned in the 'Experimental' section), this cluster being mostly P2VP and P4VP chains in the beginning. As long as we keep adding the acid, more polyanions attach themselves not only to the polycations still in solution, but also to the polycations in the exterior of the precipitate particles[18,19]. This means that on going from the lowest X_{AMPS} (0.07) to the highest (0.85), different concentrations of free pyridine rings will be found. The infra-red data confirm this interpretation of the stoichiometry of the reaction, since the intensity of the free pyridine vibrations decreases with the increase in X_{AMPS}. The results of a simple experiment that provides further support of this view are shown in *Figure 7*, where the quantity $(W_a - W_{calc})/W_{calc}$ is plotted *versus* X_{AMPS}. The actual weight of precipitate is denoted by W_a and W_{calc} is the weight calculated on the basis of exact stoichiometry between the interactive units; the mole fraction of AMPS units X_{AMPS} relates to its content in the total initial solutions of PAMPS and P2VP. (This gravimetric analysis was not possible for the blends PAMPS/P4VP due to the large waste of material during the isolation process.) It is apparent from this curve that for low X_{AMPS} the weight of precipitate is nearly twice the stoichiometrically calculated one. The value of $(W_a - W_{calc})/W_{calc}$, moreover, decreases with increase in X_{AMPS}, becomes zero for a certain composition and then increases with increasing X_{AMPS}. This last increase must be due to the presence of free sulphonic acid groups, but, unfortunately, this cannot be corroborated by infra-red studies since there is no difference between the spectrum of the sulphonic acid and sulphonate groups[15].

Also, in connection with item (4) of the previously listed spectral features of the blends, the observed reduction in intensity of the pyridine absorption could be interpreted as simply due to a dilution effect with

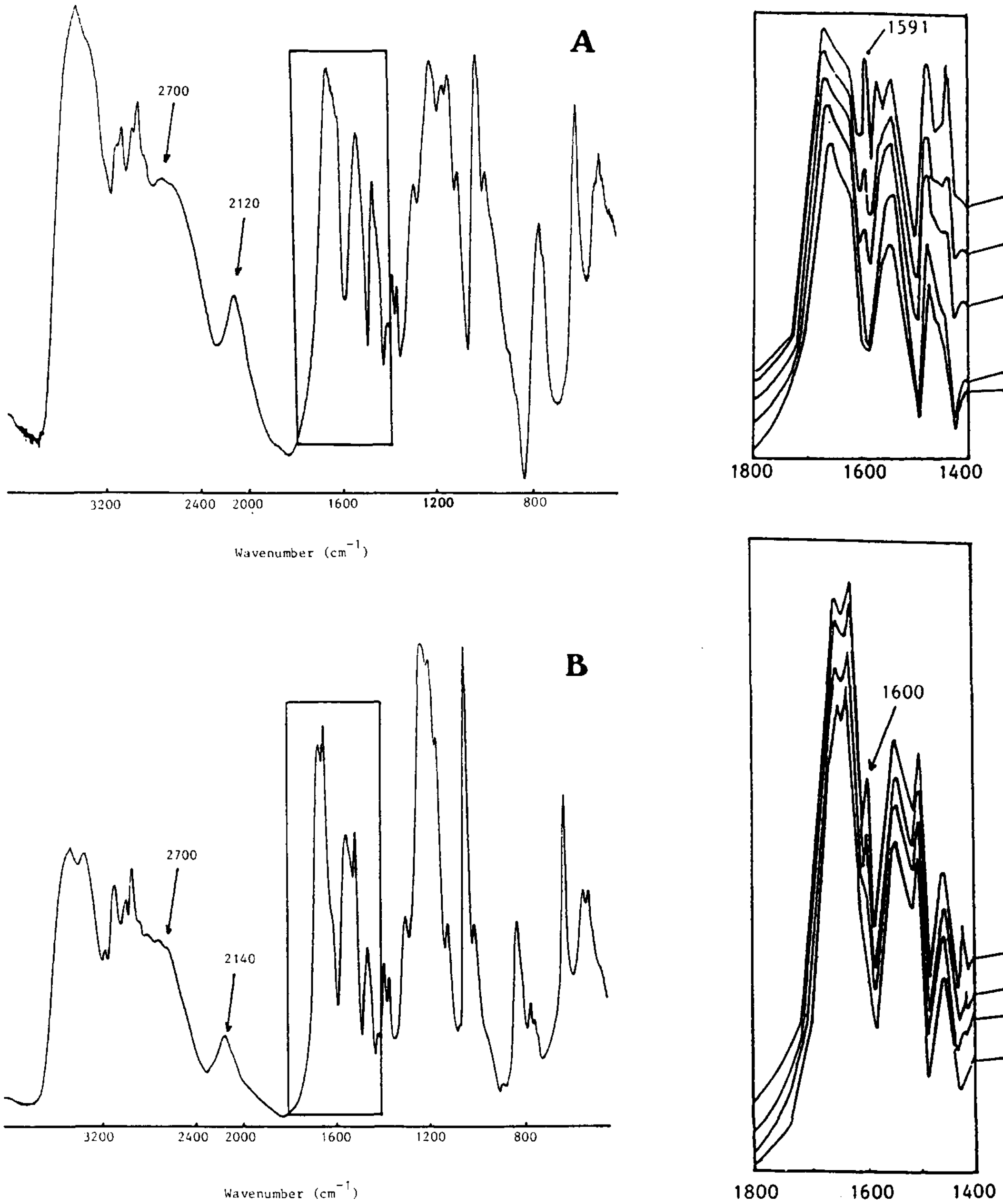

Figure 6 Infra-red spectra of the blends: (A) PAMPS/P2VP for $X_{\mathrm{AMPS}}=0.07$ (a), 0.2 (b), 0.4 (c), 0.6 (d) and 0.85 (e); and (B) PAMPS/P4VP for $X_{\mathrm{AMPS}}=0.07$ (a), 0.2 (b), 0.4 (c) and 0.6 (d)

increasing content of PAMPS. However, it must be realized that such a dilution effect has a special connotation in the present context. Thus, at medium-high values of X_{AMPS} the value of W_a is approximately equal to W_{calc} (see *Figure* 7) and it was confirmed (see *Figure 6*) that in this same region the pyridine ring absorption is undetectably small. This low absorption cannot be attributed to a very low pyridine content in the complex, since, if this were so, W_a would be less than W_{calc}, i.e. there would be negative values of $(W_a - W_{\mathrm{calc}})/W_{\mathrm{calc}}$. The fact that W_a is approximately equal to W_{calc} must be interpreted as evidence for stoichiometry of the reaction and the disappearance of pyridine ring absorption is a consequence of complete consumption of the poly(vinylpyridines).

The main spectral difference between the blends PAMPS/P2VP and PAMPS/P4VP is the satellite bands that appear at 2120 and 2140 cm^{-1}, respectively. This difference, however, does not allow one to establish unambiguously the influence of the position of the nitrogen atom within the pyridine ring on the strength of the complex formed. The strength of the interaction of PAMPS with P2VP and P4VP must depend on respective acid dissociation constants K_a of the protonated poly(vinylpyridines) (which are, of course, related to the base dissociation constant K_b). For P2VP and P4VP the values of pK_0 have been estimated to be 3.45 and 3.25 in aqueous/ethanol solutions and using HCl as titrant[20]. K_0 is the intrinsic acid dissociation constant at zero degree of protonation α (see below). These values are not entirely reliable and applicable in this case: first, because of the different nature of the solvent (30% water (v/v) in this paper), which is known to play an important role in the final behaviour due to influence on the hydrophobic interaction between base and acid[21], and, secondly, because of the fact that here the titrant is the monomer AMPS. For these reasons, we have attempted to determine the pK_0 values for P2VP and P4VP in our

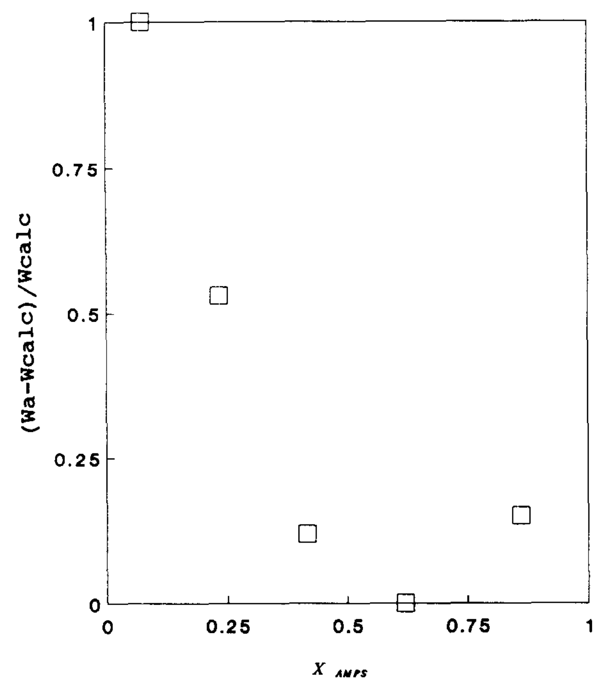

Figure 7 Change of $(W_a - W_{calc})/W_{calc}$ as a function of X_{AMPS}

conditions by means of potentiometric pH titrations. The selection of the monomer AMPS as titrant stems from the necessity to reproduce in these measurements the same kind of non-electrostatic interactions as those in the polymer blends.

The apparent dissociation constant pK_a of the protonated pyridinium rings can be estimated according to the following equation[20]:

$$pK_a = pH + \log[\alpha/(1-\alpha)] = pK_0 - (\Delta G\alpha/2.3RT) \quad (1)$$

where ΔG is the work necessary to bring a proton against the electrical field produced by the average charge of the protonated poly(vinylpyridines), R is the gas constant and T the absolute temperature. The pH values have been corrected according to the procedure of Gelsema *et al.*[22] by subtracting 0.325 from the measured value due to the fact that the calibration of the ion analyser has been carried out by using standard aqueous buffer solutions. The subtracted quantity (0.325) takes into consideration the influence of the solvent on the liquid-junction potential at the tip of the electrode. The degree of protonation has been assessed at a certain pH as the ratio of the number of moles of protonated pyridine groups to the total number of moles of pyridine groups. The number of moles of protonated pyridine groups is given by the difference between the volume of AMPS added to the P2VP and P4VP solutions (at a certain pH) and the volume of AMPS added to a blank sample (containing only solvent). The range of degrees of protonation studied here is from 0 to 0.05 due to the fact that complex and precipitant formation already occurs within this region. The addition of the monomer AMPS to the P2VP and P4VP solutions does not produce any precipitate.

Figure 8 shows the variation of pK_a as a function of α for the systems PAMPS/P2VP and PAMPS/P4VP in the protonation range 0–0.05. There are two important differences between the acid–base behaviour of P2VP and P4VP: (i) the slopes indicate a slightly larger decrease of pK_a with α for P4VP than for P2VP and (ii) the pK_0 values (obtained by linear regression) are 5.0 ± 0.1 for P2VP and 4.50 ± 0.1 for P4VP. The present results indicate that the pK_0 value for P2VP is higher than the one corresponding to P4VP for the solvent and titrant characteristics used here. These values agree qualitatively with those reported by Kirsh *et al.*[20], viz. 3.45 for P2VP and 3.25 for P4VP using aqueous ethanol (45% ethanol) solutions and HCl as titrant. The steeper slope observed for P4VP than for P2VP is a manifestation of the fact that the protonation of P4VP is somewhat more favourable thermodynamically than that of P2VP, since the slope is related to ΔG (cf. equation (1)).

Within the same range of protonation, viscometric measurements were carried out as indicated in the 'Experimental' section. *Figure 9* shows η_{sp}/C as a function of α. Here C is the concentration of poly(vinylpyridine)

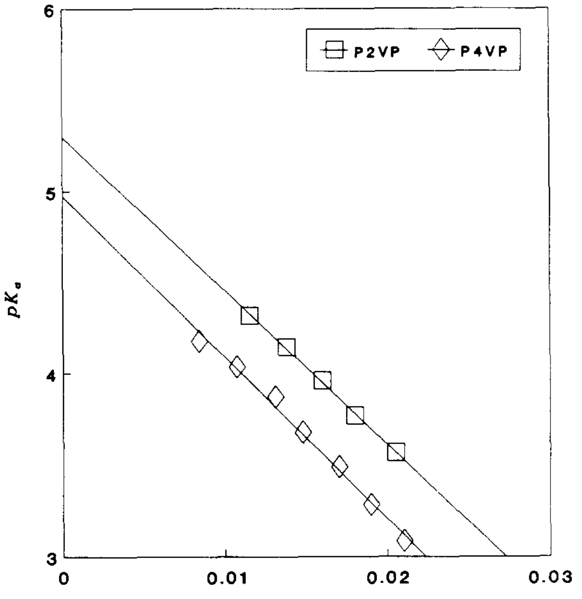

Figure 8 Variation of the apparent acid dissociation constant with the degree of protonation α

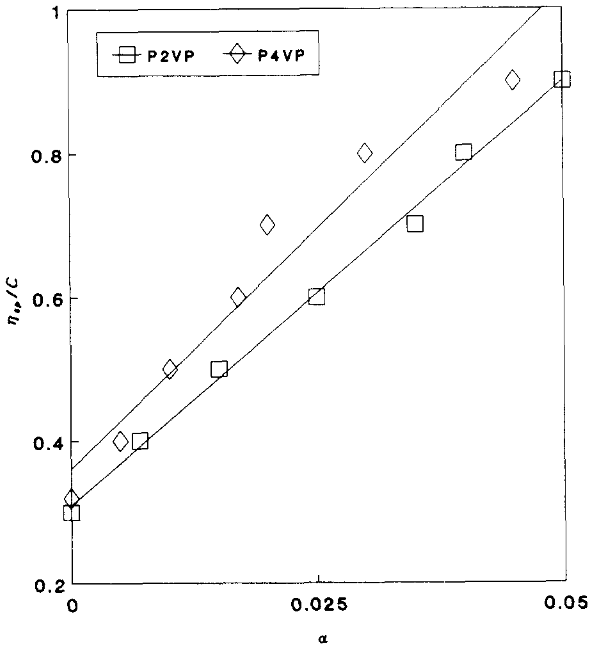

Figure 9 Reduced specific viscosity η_{sp}/C (dl g^{-1}) as a function of α

at each incremental addition of titrant. It is seen that the increase in protonation (or equivalently decrease in pK_a) is accompanied by an increase in the η_{sp}/C values. This indicates a large expansion of the macromolecules on addition of the acid AMPS (the same effect was observed by Kirsh *et al.*[20] for similar systems).

It is possible, therefore, to state that under the experimental conditions used here, P2VP is slightly more basic than P4VP. This must be associated with the position of the satellite peaks observed in the complex at 2120 cm^{-1} for the system PAMPS/P2VP and at 2140 cm^{-1} for the system PAMPS/P4VP, which is the significant difference between the two systems observed by infra-red spectroscopy. The expansion of the macromolecules when the acid is added to the polybase solutions, shown by viscosity measurements, suggests a possible answer to the question why the two polymers precipitate when they form the complex. The protonation of the pyridine ring when PAMPS is added gives rise to strong repulsive interactions between positively charged pyridine rings. However, contrary to what happens when the monomer is poured into the poly(vinylpyridine) solutions, reduction of these repulsions by chain expansion cannot take place due to the existence of an effective crosslinking (and reduction in degrees of freedom and entropy) brought about by the chain-like character of both interactive species, with subsequent insolubility.

Finally, the calorimetric analysis of these blends in *Table 1* shows evidence of some interesting behaviour for both PAMPS/P2VP and PAMPS/P4VP. If we take account of the glass transition T_g displayed for the homopolymer PAMPS (see *Figure 5*) at 348 K and of the glass transitions at 373 and 423 K for P2VP and P4VP, respectively, the most noticeable thermal features found for these blends are as follows:

(1) In all cases the blends display only one T_g.

(2) The T_g values corresponding to the blends are higher than those found for the individual components.

(3) The molecular weight is of unexpected importance, as can be drawn from the behaviour shown by the blend PAMPS/P2VP-1 and PAMPS/P2VP-2. The former displays a higher T_g than the latter although both homopolymers P2VP have the same T_g. It will be recalled that the molecular weights of P2VP-1 and P2VP-2 are 1.6×10^5 and 0.4×10^5 g mol^{-1}, respectively.

(4) The difference T_g(blend) − T_g(poly(vinylpyridine)) is always bigger for the system PAMPS/P2VP than for the system PAMPS/P4VP.

The first feature indicates that we are dealing with systems where strong interactions are taking place. These strong interactions give rise to a large decrease in the free volume, with regard to the constituent homopolymers, and therefore the T_g values of the final products are larger. The second one, however, represents a source of controversy, since it implies that the known rule of thumb that establishes that two polymers are miscible if the T_g values of blends are intermediate between those of the single components does not apply in these cases. Similar thermal behaviour has been reported by Lee *et al.* on the system poly(2-vinylpyridine)/poly(vinylphenol)[4]. The glass transitions of the homopolymers for this latter blend were reported to be located at 427 K for poly(vinylphenol) and 356 K for P2VP, whereas the glass transition for the complex was found at 443 K. The influence of molecular weight is another surprising result. The cause of this effect has been considered, but we have been unable to provide a wholly satisfactory explanation. It is planned to explore the matter further by synthesizing and using samples of both PAMPS and poly(vinylpyridines) encompassing a very wide range of molecular weights. Finally, the higher values of the difference T_g(blend) − T_g(poly(vinylpyridines)) for PAMPS/P2VP than for PAMPS/P4VP suggest a somewhat bigger strength of the interaction between both homopolymers for the former, which supports the results found by infra-red and titration techniques.

Table 1 Glass transition temperatures (K) of the blends PAMPS/P2VP and PAMPS/P4VP

X_{AMPS}	PAMPS/P2VP-1	PAMPS/P2VP-2	PAMPS/P4VP
0.0	369	374	422
0.07	438	408	441
0.20	435	412	440
0.40	433	408	439
0.60	457	403	439
0.85	455	405	439
1.0	358	358	358

ACKNOWLEDGEMENTS

One of the authors (J.M.R.) is grateful for the financial support provided by the Ministerio de Educación y Ciencia of the Spanish Government.

REFERENCES

1 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
2 Robeson, L. M. *Polym. Eng. Sci.* 1984, **24**, 587
3 Schmitt, B. T. *Angew. Chem., Int. Edn. Engl.* 1979, **18**, 273
4 Lee, J. Y., Moskala, E. J., Painter, P. C. and Coleman, M. M. *Appl. Spectrosc.* 1986, **40**, 991
5 Lee, J. Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1988, **21**, 954
6 Abe, K., Hiroyuki, O. and Tsuchida, E. *Makromol. Chem.* 1977, **178**, 2285
7 Cesteros, L. C., Rego, J. M., Vazquez, J. J. and Katime, I. *Polym. Commun.* in press
8 Cowie, J. M. G., Garay, M. T., Lath, D. and McEwen, I. J. *Br. Polym. J.* 1989, **21**, 81
9 Smid, J. and Fish, D., Polymer electrolytes, 'Encyclopedia of Polymer Science and Engineering', John Wiley, New York, 1979, Vol. 11, pp. 720–39
10 Reillex Report 3, Reilly Chemicals SA, Brussels, Belgium
11 Laskey, R. A., US Patent 3929741, 1975
12 Schulz, D. N., Peiffer, D. G., Agarwal, P. K., Larabee, J., Laladas, J. J., Soni, L., Handwerker, B. and Garner, R. T. *Polymer* 1986, **27**, 1734
13 Fisher, L. W., Sochor, A. R. and Tan, J. S. *Macromolecules* 1977, **10**, 949
14 Arichi, S. *Bull. Chem. Soc. Japan* 1966, **39**, 439
15 Bellamy, L. J. 'The Infrared Spectra of Complex Molecules', Methuen, London, 1960, Ch. 22
16 Lee, W. A. and Rutherford, R. A. in 'Polymer Handbook', 2nd Edn. (Eds. J. Brandrup and E. H. Immergut), Wiley, New York, 1975, Ch. III, p. 139
17 Odonikov, S. E., Mashkovsky, A. A., Glazunov, V. P., Iogansen, A. V. and Rassadin, B. V. *Spectrochim. Acta* (*A*) 1976, **32**, 1355
18 Fuoss, R. M. and Sadek, H. *Science* 1949, **110**, 552
19 Michaels, A. S. and Miekka, R. G. *J. Chem. Phys.* 1961, **65**, 1765
20 Kirsh, Y. E., Komarova, O.P. and Lukovkin, G. M. *Eur. Polym. J.* 1973, **9**, 1405
21 Satoh, M., Yoda, E., Hayashi, T. and Komiyama, J. *Macromolecules* 1989, **22**, 1808
22 Gelsema, W. J., De Ligny, C. L., Remijnse, A. G. and Blijleven, H. A. *Recl. Trav. Chim. Pays-Bas* 1966, **85**, 647