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Infrared Spectroscopic Study of Blends of Poly(styrene-*co*-styrenesulfonic acid) with Poly(styrene-*co*-(4-vinylpyridine))

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ABSTRACT: Poly(styrene-*co*-styrenesulfonic acid) copolymers containing 2–10 mol % acidic units were mixed in stoichiometric amounts of interacting groups with poly(styrene-*co*-(4-vinylpyridine)) copolymers containing 2–10 mol % basic units. FTIR spectroscopy revealed that ca. 80–90% of the pyridine units in the blend were protonated, with the pyridinium ions H-bonded to the anion. An FTIR temperature study indicated that the pyridinium units were involved in an equilibrium involving the H-bonded pyridinium/sulfonate ion pair and most likely the H-bonded but nonionic acid/base pair. Previously reported mechanical property measurements were interpreted in light of these results.

Introduction

It is generally accepted that most mixtures of polymers are not miscible because of their unfavorable heats of mixing. This situation can be reversed by the introduction into the polymers to be mixed of complementary interacting units A and B. (In this context, units A and B are said to be complementary when the interaction between the unlike A and B moieties is much stronger than that between like moieties.) The moieties can be chosen to result in H-bond formation, proton transfer, charge transfer, electron donor/acceptor interactions between electron rich and electron deficient species, or even covalent bonds.

Proton transfer has been used several times in our laboratory to enhance the miscibility of otherwise immiscible polymer/polymer and polymer/plasticizer mixtures.[1–4] It would be useful to study and quantify the extent of this interaction in a uniform polymer matrix where any interaction between the reactive moieties is not thermodynamically hindered by the dissimilar nature of the backbones of the polymers being mixed. Consequently, this paper reports on the type of interaction present in blends of poly(styrene-*co*-4-vinylpyridine) copolymers with poly(styrene-*co*-styrenesulfonic acid) copolymers, where the only difference between these blends and PS is the presence of interacting groups.

Experimental Section

In the text that follows, it will be useful to refer to chemical units by various acronyms: 4VP = 4-vinylpyridine, 4VPH$^+$ = the 4-vinylpyridinium (protonated 4VP) ion, S = styrene, SSA = styrenesulfonic acid, S-SSA = styrene-*co*-styrenesulfonic acid copolymer, S-4VP = styrene-*co*-4-vinylpyridine copolymer, S-4VPH$^+$ClO$_4^-$ = perchloric acid salt of S-4VP.

Polymer Synthesis. S-4VP copolymers of 2–10 mol % 4VP content as well as their perchloric acid salts were obtained through the courtesy of Dr. Sylvie Gauthier. Their preparation is discussed elsewhere.[5] Viscosity average molecular weights of these were evaluated at about 1×10^5.

Polystyrene (Polysciences) having an average molecular weight between 125 000 and 250 000 was sulfonated using a procedure suggested by the patent of Makowski et al.,[6] resulting in S-SSA copolymers having SSA contents of 2–10 mol %. Sulfonation of the benzene ring is claimed to occur at random at the para position. Polymers were dried at 90 °C overnight and kept at 50 °C under vacuum until required. The acid group content was determined by titration of a solution of the polymer in a benzene/methanol (90/10; v/v) mixed solvent with dilute methanolic NaOH solution under a positive pressure of nitrogen, using phenolphthalein as an indicator.

Table 1. Comonomer Content (in mol %) of the S-SSA and S-4VP Copolymers Used in the Preparation of the Blends

2% blend		5% blend		7% blend		10% blend	
% SSA	% 4VP	% SSA	% 4VP	% SSA	% 4VP	% SSA	% 4VP
1.8	1.9	5.1	5.2	6.4	7.2	9.9	9.9

The nomenclature used in referring to the composition of copolymers is based on that suggested by Eisenberg and King;[7] for example, a copolymer of monomer A with monomer B containing 5.2 mol % of monomer B would be referred to as copolymer A-0.052B.

Blend Preparation. Copolymers having similar SSA and 4VP contents were dissolved separately in tetrahydrofuran (THF) (4% w/w), and the solutions were mixed by the dropwise addition of one to the other under vigorous stirring. The mixtures were agitated for 15 min, followed by solvent evaporation. The resulting product was dried in a vacuum oven at 70 °C for 1 week and remained there at 50 °C until required. Blends were prepared so as to contain stoichiometric amounts of interacting groups. Mixing was accompanied by the formation of a gelatinous precipitate which would hinder the stirring action of the magnetic bar. Hence, stirring was continued by the manual swirling of the solution flask. Blends will be referred to by the approximate comonomer content of the constituents; for example, the blend resulting from the addition of a S-0.047SSA copolymer to a S-0.053 4VP copolymer will be referred to as a 5% blend. The exact composition of the copolymers used in the preparation of the blends is given in Table 1.

Thin films (thickness <0.1 mm) for IR measurements were prepared by molding at a temperature of $T_g + 30$ deg for about 10 min at a pressure of approximately 4 MPa.

IR Spectroscopy. IR spectra were obtained on a Nicolet 7000 series Fourier transform IR spectrometer. Typically, 32 interferograms taken at a rate of one per second were averaged to yield a spectrum of 4-cm^{-1} resolution. Film thickness was controlled to ensure that the absorbance of relevant bands would not exceed 1.4; this relatively high value was observed in the pure copolymers of highest comonomer contents (mol ratio = 0.10) only. Absorbances were calculated by averaging peak heights of five sets of scans taken over different areas of the polymer film.

Absorbance measurements were converted to functional group content in the following fashion. First, the absorbance spectra of a series of S-4VPH$^+$ClO$_4^-$ copolymers of various known 4VPH$^+$

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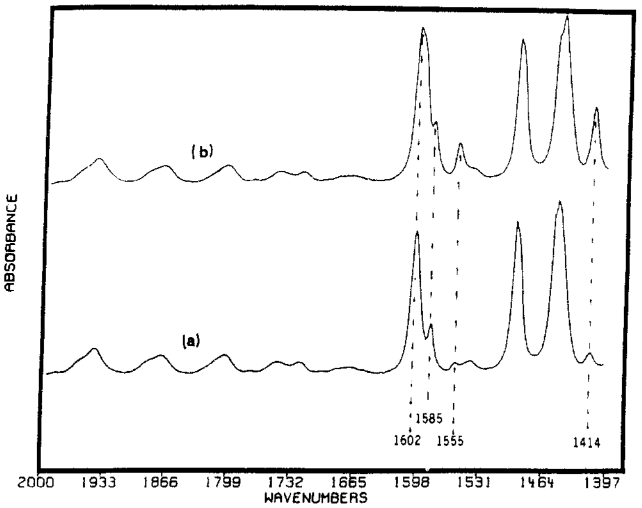

Figure 1. IR spectra of (a) S-0.021 4VP and (b) S-0.101 4VP copolymers.

contents were obtained, and characteristic bands for $4VPH^+$ and for S were identified. If A_{4VPH^+} and A_S represent the peak absorbances of these two bands, application of the Beer–Lambert law yields

$$A_{4VPH^+}/A_S = (\epsilon_{4VPH^+}/\epsilon_S)([4VPH^+]/[S])$$

where ϵ_X is the molar absorptivity and [X] the concentration of absorbing species X in moles per unit volume. It should be noted that the concentration ratio is identical to the mole ratio. The ratio of the molar absorptivities is expected to be a constant when the molecular environment stays approximately the same. It will be assumed for now that this is the situation in the copolymers studied. Consequently, for a given series of S-$4VPH^+ClO_4^-$ copolymers, linearity would be expected when plotting the A_{4VPH^+}/A_S ratio vs the $4VPH^+$/S mole ratio. The spectrum of a blend of unknown $4VPH^+$/S mole ratio can then be obtained and its measured A_{4VPH^+}/A_S value interpolated on the calibration curve described above to obtain this ratio.

Polymer spectra were recorded as a function of temperature with a Mettler FP52 hot-stage regulated by a Mettler FP5 temperature control unit. Spectra of the 5, 7, and 10% blends were taken every 5–10 deg with the hot-stage temperature increasing at a rate of approximately 2 deg/min, over the 25–275 °C range, the upper temperature for these measurements being limited by sample flow. Care was taken so as to ensure that the film was not under tension in the furnace. Each polymer spectrum was ratioed to a background spectrum taken at the same temperature. This was accomplished by heating the empty hot-stage and collecting background spectra at various temperatures prior to inserting the polymer film into the hot-stage.

Results and Discussion

IR Spectroscopy of the Copolymers. The reader is cautioned that in the spectra that follow, two prominent bands sometimes appear (at 1777 and 1722 cm^{-1}) which are remnants of the film preparation procedure and were later found to disappear upon heating at 100 °C for 1 h. The band at 1722 cm^{-1} is due to THF, which absorbs very strongly at 1726 cm^{-1} in the pure form. The band at 1777 cm^{-1} is of unknown origin. They will be identified by an asterisk in the spectra presented. Both these bands are relatively small and removed from the location of those bands whose peak absorbance was measured. Consequently, their presence did not affect the precision of our measurements. We also feel that the presence of small amounts of THF would not greatly affect the nature nor the extent of the interaction in the blends, except possibly if it were to solvate any ionic species.

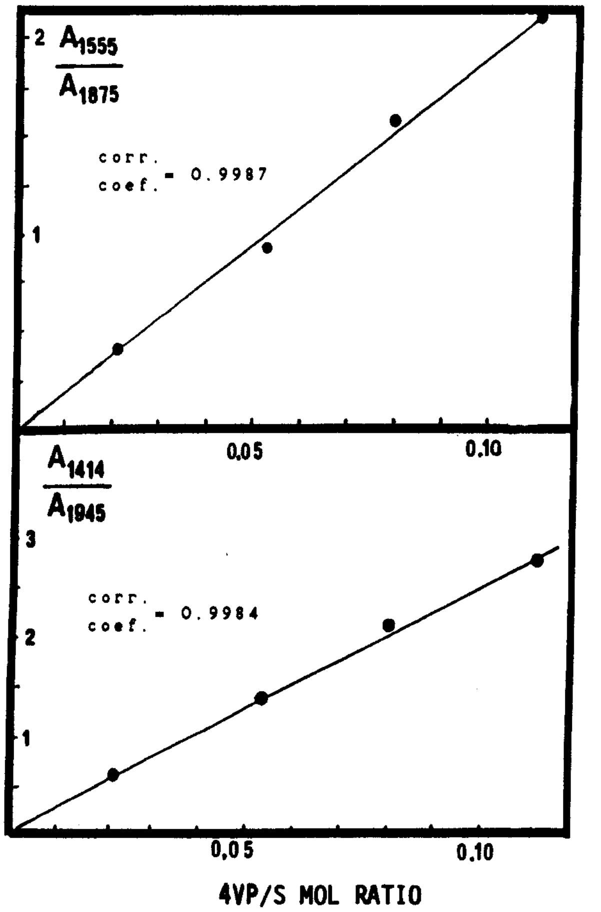

Figure 2. Calibration curves relating the ratio of 4VP to S band absorbances to copolymer composition for the series of S-4VP copolymers.

Analysis of 4VP Content in S-4VP Copolymers. Spectra of the S-4VP copolymers (Figure 1) revealed bands at 1555 and 1414 cm^{-1} whose intensities were directly proportional to the 4VP content. Bands have also been seen at these locations in the spectra of P4VP[8] and its low molecular weight (MW) analog, 4-isopropylpyridine.[9] In both of these compounds, there also appears a strong band located at 1596 cm^{-1}. This band likely manifests itself in the S-4VP spectra as a gradual blurring of the minimum between the two S bands located at 1602 and 1585 cm^{-1}.

The 1555-cm^{-1} band has been reported as being due to the C=C stretch in the pyridine ring.[10] The 1596-cm^{-1} 4VP vibration has been assigned to the C=N stretch in the pyridine ring[10] and has been reported at 1602 cm^{-1} in ethyl acrylate–4VP copolymers.[11] Its position, i.e. situated between two S peaks, renders its quantitative evaluation difficult, though it will be useful as a qualitative indicator.

The PS bands used as internal standards were those at 1945 and 1875 cm^{-1}.[12,13] The ratio of the 4VP and S band absorbances was tabulated for two combinations of 4VP and S bands; the results are plotted in Figure 2. The first of these curves will be our 4VP/S calibration curve for the remainder of this study.

On each graph is listed the correlation coefficient for the least mean squares fit. The linear behavior of the data can be taken as an indication that the ratio of the molar extinction coefficients, $\epsilon_{4VP}/\epsilon_S$, is, within the precision of the experiment, constant over the range of compositions studied.

Analysis of $4VPH^+$ Content in S-$4VPH^+ClO_4^-$ Copolymers. The spectra of two S-4VP perchlorate salts are presented in Figure 3. Neutralization leads to the total disappearance of the 1414- and 1555-cm^{-1} 4VP bands and to the appearance of a prominent new peak located

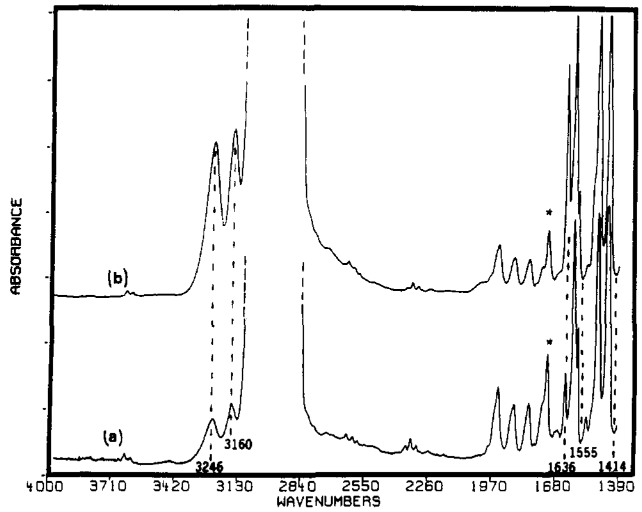

Figure 3. IR spectra of the perchlorate salts of (a) S-0.021 4VP and (b) S-0.095 4VP copolymers.

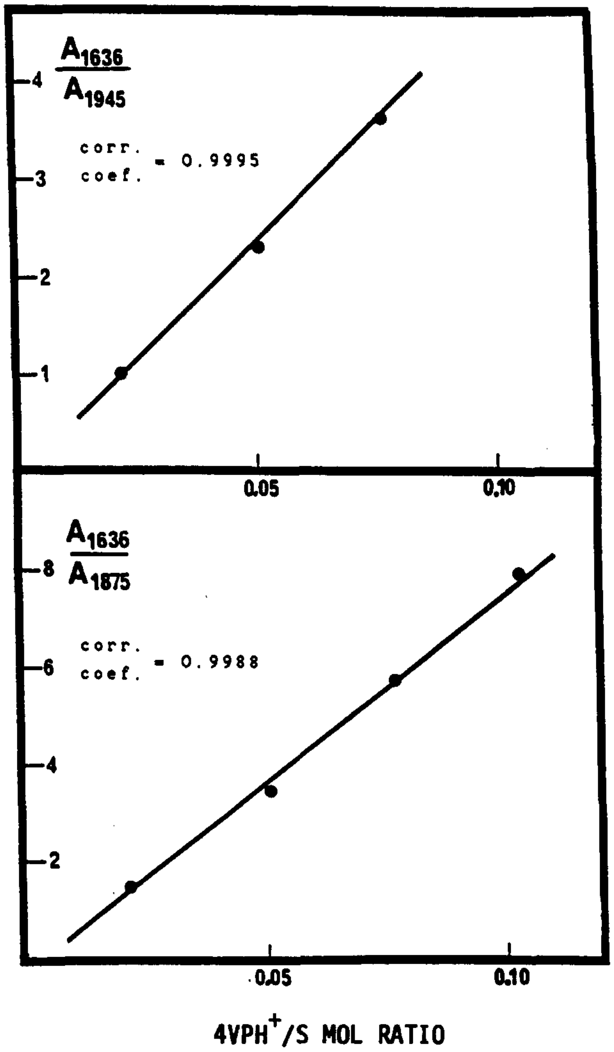

Figure 4. Calibration curves relating the ratio of $4VPH^+$ to S band absorbances to copolymer composition for the perchlorate salts of the series of S-4VP copolymers.

at 1636 cm^{-1}. This band is always present in salts of pyridine[14,15] and P4VP[16] and is said to involve nuclear vibrations of the pyridinium ring.[15]

The ratios of the $4VPH^+$ 1636-cm^{-1} band absorbance to that of two S bands are presented in Figure 4 for the series of S-4VP salts. The linearity of the data indicates that the ratio of the extinction coefficients of interest, $\epsilon_{4VPH^+}/\epsilon_S$, does not vary across the copolymer composition range examined.

Close inspection of these spectra reveals that the minimum between the 1602- and 1585-cm^{-1} styrene peaks has been made sharp again upon protonation of the 4VP units, possibly indicating that while 4VP absorbs at slightly less than 1602 cm^{-1}, protonated 4VP does not. Indeed, Panov observed a decrease in the 1596-cm^{-1} pyridine band intensity upon partial complexation of P4VP with perchloric acid.[16]

Further removed from this region was the appearance of a sharp doublet at 3246 and 3160 cm^{-1}, the relative intensity of which was found to be proportional to $4VPH^+$ content. There appeared also a very weak band at 2025 cm^{-1} in the highest ion content salt only. The significance of these bands will now be discussed.

The frequency of the N–H stretching mode vibration in pyridine salts is known to depend on whether H-bonding occurs between the NH^+ group and the accompanying counterion. Simple pyridine salts may be devided into two groups, depending on whether there is H-bonding between the pyridinium ion and the anion.[17] When there is H-bonding, the N–H stretch appears as a single broad feature in the 2400–3000-cm^{-1} region, sometimes accompanied by one or two sharp bands near 2000 cm^{-1}.

In the absence of H-bonding, it appears as a series of 2–4 sharp band slying between 3400 and 3100 cm^{-1}. For perchloric acid salts of pyridine, these bands have been seen at 3268, 3195, and 3118 cm^{-1},[17] while they appeared at 3260, 3170, and 3100 cm^{-1} for perchlorate salts of P4VP.[16] Clearly then, the pyridinium ions are not H-bonded to the anion in the perchlorate salts of the S-4VP copolymers.

Analysis of SSA Content in the S-SSA Copolymers. The IR spectra of the S-SSA copolymers have been previously reported in the literature. With respect to the present paper, the recent work of Sakurai et al. is especially informative on this topic.[11] There is no need in this study to attempt to evaluate the extent of SSA deprotonation in the blends because we will concentrate on evaluating the extent of 4VP protonation. Since SSA is the only strong acid in the blends, the amount of deprotonated SSA can be inferred from the amount of protonated 4VP in the blend. Furthermore, more precise measurements are possible on bands associated with $4VPH^+$ than with SSA because of the intensity and location of the bands involved.

Analysis of S Content in S-Based Copolymers. The 1945- and 1875-cm^{-1} bands of PS, assigned to combination vibrations and overtones of the benzene ring,[13] were used as internal standards in the various calibration curves presented here. Previous studies on P4VP[8] and its low MW analog, 4-isopropylpyridine,[9] indicate that the 4VP unit does not absorb in this region, nor do its salts.[16] However, the SSA units may conceivably absorb in this region. It is well-known that substitution of benzene causes a change of absorpton in the 2000–1660-cm^{-1} region.[18] If the spectrum of monosubstituted benzene is compared to that of para disubstituted benzene in the 1800–1900-cm^{-1} region, it is generally found that while the former possesses a band a 1875 cm^{-1}, the latter possesses a band at 1885 cm^{-1}. Although the expected SSA 1885-cm^{-1} band will probably contribute to the measured absorbance of the 1875-cm^{-1} S band, it must be realized that the content of SSA relative to that of S in the blends will vary from 1 to 6% and that its only contribution would be as a shoulder to the 1875-cm^{-1} peak. It must further be noted that the presence of a significant contribution is indeed doubtful due to the experimentally observed constancy of the 1875-

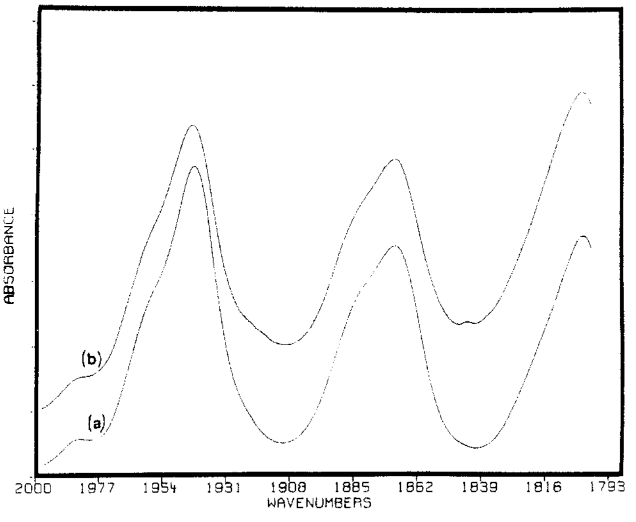

Figure 5. IR spectra of (a) PS and (b) a S-0.064 SSA copolymer in the 2000–1800-cm^{-1} region.

cm^{-1} S peak shape over the series of S-SSA copolymers studied, as shown in Figure 5.

Other Bands of Interest. H-Bonded 4VP. Given the tendency of pyridine to form H-bonds with weak acids, one must be aware of the location of bands indicative of such interactions. For pyridine, the 1585-cm^{-1} ring mode vibration shifts up by 18 cm^{-1} upon formation of a H-bond with weak acids[14] while the 1590-cm^{-1} ring mode of the pyridine group in P2VP shifts upward by 10 cm^{-1} upon interacting with a carboxylic acid.[19] Such changes will not be of great concern to us, as will become obvious later. Suffice it to say that the 1596-cm^{-1} band of 4VP could reasonably be expected to shift up by about 10–20-cm^{-1} upon H-bond formation.

Spectral bands connected with the O–H section of the acidic species would also be affected upon H-bond formation with pyridine. In the absence of spectra of sulfonic acids H-bonded to pyridine, insight on the frequency of these bands may be gained from spectra of mixtures of carboxylic acids with pyridine. For these, two broad bands appear which are typically centered around 2500 and 1900 cm^{-1};[20] they are related to vibrations of the H-bonded O–H unit. It must be stressed, however, that bands in this area cannot be unequivocally assigned to an H-bonding interaction occurring in the pyridine/acid pair without other supporting evidence, since many other H-bonded pairs absorb in this region. For example, in poly(acrylic acid) grafted onto PTFE, low intensity broad bands show up at 2650 and 1970 cm^{-1} and are assigned to Fermi resonance enhanced overtones and combinations of vibrations involving the dimerized acid O–H unit;[21] H-bonded sulfonic acids may also show such bands. Indeed, sulfonic acids have been shown to be active in this area: the acid form of Nafion has an intense and broad band at 2750 cm^{-1}, which is assigned to acid protons involved in very strong H-bonds,[22] while H-bonded SSA has been found to absorb at 2405 cm^{-1}.[23] Finally, as mentioned previously, the N–N stretch of 4VPH$^+$ also appears in this region when the cation is H-bonded to the anion.

H_2O Bands. Ionomers tend to attract water molecules. Several studies have appeared on the IR spectra of ionomers containing water (see, for example, refs 13 and 22–24). Water can typically show up at 3620 cm^{-1} (the O–H stretch of non-H-bonded water), at ca. 3420 cm^{-1} (the O–H stretch of H-bonded water in pure water), in the 3460–3200-cm^{-1} range (the O–H stretch of H-bonded water in ionomers), and around 1640 cm^{-1} (a scissor mode). The spectra of the S-SSA copolymers all had a broad band at 1697 cm^{-1}, that we assign to the scissor mode of water molecules H-bonded to sulfonic acid units by comparison with the work of Leuchs and Zundel[25] who assigned the 1685-cm^{-1} band in aqueous solutions of benzenesulfonic acid to this mode. All the other polymers studied, including the blends, showed no evidence of water activity.

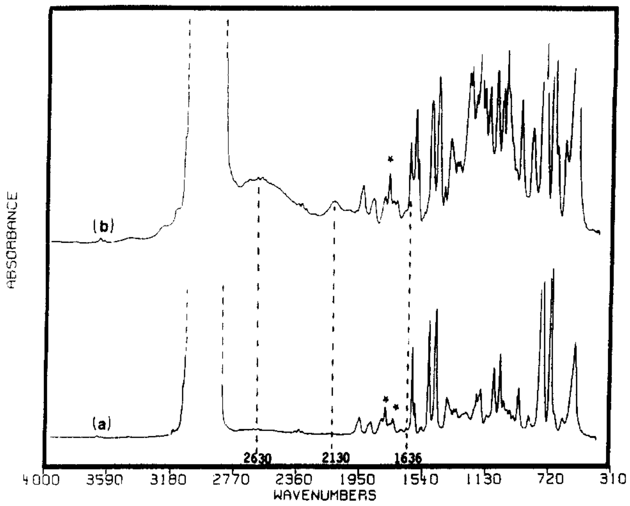

Figure 6. IR spectra of (a) the 2% blend and (b) the 10% blend.

Table 2. Characteristic IR Bands for Various Functional Units in the 1400–3300-cm^{-1} Region

PS	1585, 1602, 1875, 1945
4VP	1414, 1555, 1596
4VPH$^+$	
H-bonded	1636, broad band in the 2400–3000 region
free	1636, 2–4 sharp bands in the 3100–3400 region

The IR band positions of the various species of interest are summarized in Table 2.

IR Spectroscopy of the Blends. The IR spectra of the 2 and 10% blends are presented in Figure 6, while Figure 7 presents a summary overview of the 2200–1500-cm^{-1} regions of the spectra discussed so far. As the interacting group content increases in the blends, the following band intensities are seen to increase: (1) a very broad band near 2630 cm^{-1}, of half-width of approximately 400 cm^{-1}; (2) a broad band near 2130 cm^{-1}, of approximately 60-cm^{-1} half-width; (3) a weak broad band at 2024 cm^{-1}, of intensity one-tenth that of the 2130-cm^{-1} band, seen also as an extremely weak band in the S-4VP perchlorate salts; (4) a sharp band at 1636 cm^{-1}, previously assigned to a ring vibration of the pyridinium ion; (5) a weak shoulder at 1520 cm^{-1} for the highest interacting group content only and which was previously observed upon protonation of the S-4VP copolymers by $HClO_4$. Such broad bands as those observed in the 2700–1900-cm^{-1} region are often found to occur for systems where H-bonds involving acids or protonated amines are present, including those where the pyridinium ion is H-bonded to the counterion.

In the spectra of the blends, there was also much information to be gained from the absence or near-absence of certain bands. These include (1) the two sharp bands around 3200 cm^{-1} seen in the spectra of the perchlorate salts of the S-4VP copolymers and assigned to the N–H stretch of non-H-bonded pyridinium ions and (2) the 1555-cm^{-1} band assigned to a ring vibration of 4VP, which also dissappeared upon protonation of the 4VP units by $HClO_4$.

A few conclusions can be drawn from the spectral information obtained: (1) There are very few free 4VP units in the blends; i.e. the great majority of 4VP units are participating in some type of interaction which changes the frequency of the 1555-cm^{-1} 4VP vibration. (2) Nearly

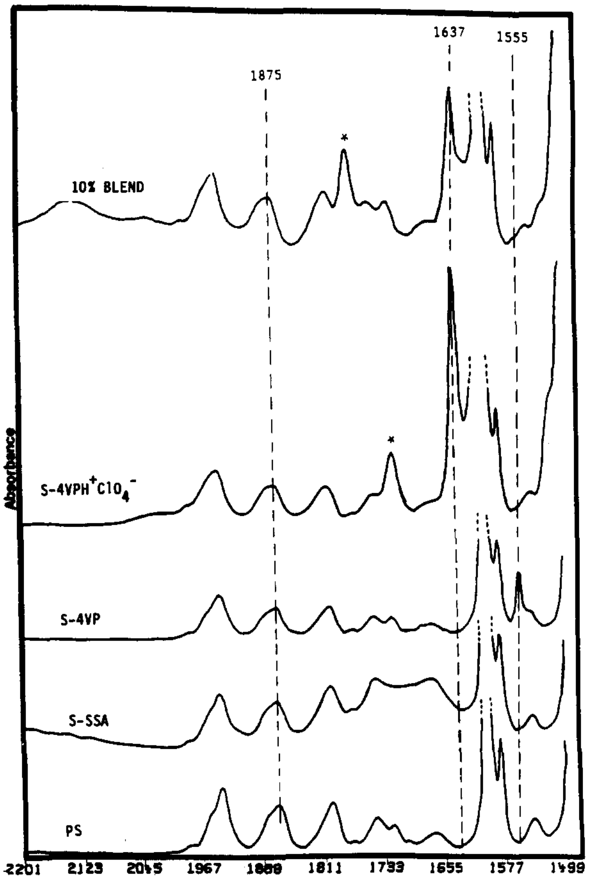

Figure 7. IR spectra of PS, the S-0.064 SSA and S-0.101 4VP copolymers, the perchlorate salt of S-0.095 4VP, and the 10% blend.

Table 3. Composition of Blends, Expressed in Mole Ratio, and Extent of 4VP Protonation, As Measured by FTIR

% blend	$[4VP]_{TOT}$/[S]	$[SSA]_{TOT}$/[S]	$4VPH^+$]/[S]	protonation efficiency (%)
2	0.0101	0.0087	a	a
5	0.0266	0.0272	0.0222 ± 0.0044	83 ± 16
7	0.0362	0.0363	0.0293 ± 0.0040	81 ± 11
10	0.0557	0.0541	0.0471 ± 0.0036	87 ± 7

[a] Uncertainty too large to render a significant result.

all the pyridinium ions produced in the blends are H-bonded to the sulfonate ion.

For the blends, it was possible to evaluate the 4VP/S and $4VPH^+$/S mole ratios through measurement of the A_{1555}/A_{1875} and A_{1636}/A_{1875} ratios, respectively, using the calibration curves previously prepared. The 1636-cm^{-1} peak baseline consisted of a horizontal line coinciding with many minima in the vicinity. The 1875-cm^{-1} peak baseline consisted of a slightly slanted line linking the 2000- and 1840-cm^{-1} data points, the slant being due to the broad 2130-cm^{-1} peak. The validity of this baseline was tested by taking the ratio of the intensities of two S bands situated between 2000 and 1840 cm^{-1}; for all the blends, the A_{1875}/A_{1945} ratio was found to be 0.71 ± 0.01.

For each of the blends, the value of $[4VP]_{TOT}/[S]$, where $[4VP]_{TOT}$ represents the total concentration of 4VP units in all possible forms, was calculated, together with the $[SSA]_{TOT}/[S]$ ratio. The protonation efficiency, defined here as the ratio of the number of protonated 4VP units to the maximum possible value, was obtained by dividing the graphically determined $[4VPH^+]/[S]$ value by the smaller of the $[4VP]_{TOT}/[S]$ and $[SSA]_{TOT}/[S]$ values. These results are presented in Table 3.

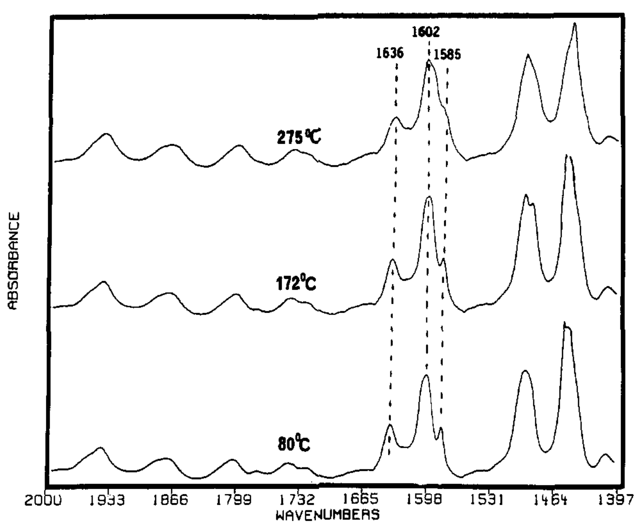

Figure 8. IR spectra of the 10% blend at various temperatures.

According to the data presented in Table 3, the 7 and 10% blends theoretically contain amounts of unprotonated 4VP which correspond to [4VP]/[S] ratios of 0.007. Experimentally, values of 0, 0.004 ± 0.002 and 0.003 ± 0.002, were determined for this series. It is to be noted that the location of the 1555-cm^{-1} peak as a shoulder on a S band at 1547 cm^{-1} hinders greatly the precision of this method when the [4VP]/[S] ratio is lower than approximately 0.01; indeed, the limit of detection is of the order of 0.003. As a result, it is impossible to ascertain with precision the fraction of the 4VP units which are being "seen" by our measurement of the 1555-cm^{-1} band absorbance characteristic of free 4VP units.

In summary, the IR measurements indicate that of the order of 80–90% of the 4VP units in the blends are protonated. This level of interaction is similar to what has been observed in blends of S-SSA with poly(ethyl acrylate-*co*-4-vinylpyridine) for which the approach of the interacting units was thermodynamically hindered by the immiscibility of the PS/poly(ethyl acryalte) pair.[11,26] There is little experimental proof to confirm the state (free or H-bonded) of the unaccounted 4VP units. Furthermore, nearly all of the pyridinium units are H-bonded to the sulfonate anions, so that these two ions must necessarily be in close proximity. Hence, any solvating effect by residual THF was minimal.

Temperature Dependence of IR Spectra. The spectra of the 5, 7, and 10% blends were recorded as a function of temperature. Upon heating, little change occurred in the spectra until approximately T_g, at which point two important changes manifested themselves. Although the onset of change was relatively sudden, the changes themselves were progressive. As shown in Figure 8, these included a relative decrease in the 1636-cm^{-1} peak height and the disappearnce of the minimum located between the S peaks at 1602 and 1585 cm^{-1}. Conspicuous by its absence is the expected 1555 cm^{-1} peak associated with free 4VP, which was seen to remain invariant in the spectra of S-4VP copolymers even when these were heated to 200 °C.

For each blend, the $[4VPH^+]/[S]$ ratio was calculated at several temperatures from the A_{1636}/A_{1875} ratio and the previously constructed calibration curve. Implicit in this approach is that the extinction coefficients of the two bands do not vary greatly with temperature or, if they do, that their ratio does not. The fraction of 4VP units which are protonated, p, was then calculated as $\{[4VPH^+/[S]\}/\{[4VP]_{TOT}/[S]\}$. At the highest temperatures studied, p

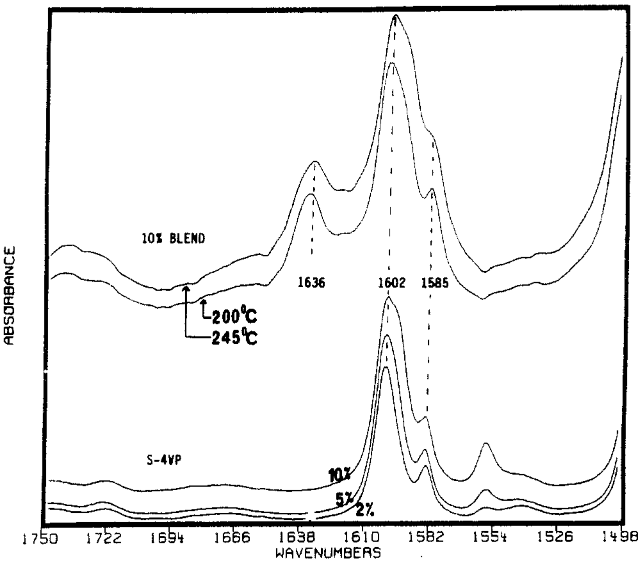

Figure 9. IR spectra of the 10% blend at high temperatures and of several S-4VP copolymers at room temperature. Numbers beside the curves refer to the 4VP mol % content of the copolymers.

typically decreased to values of approximately 0.65, a value not small enough to result in a clearly observable 4VP band.

Figure 9 presents the spectra of several S-4VP copolymers at room temperature together with that of the 10% blend at high temperatures. The intensity of the interference in the 1600-cm^{-1} region which is causing the disappearance in the blend of the minimum between two S bands at high temperatures is anomalously strong. Upon inspection of Figure 9, it can be inferred that if this interference were caused by free 4VP absorbing at its characteristic 1596-cm^{-1} frequency, it would require a higher [4VP]/[S] ratio in the blend than its calculated $[4VP]_{TOT}/[S]$ ratio. Consequently, free 4VP is not responsible for the interference. An alternative explanation is that it is caused by a broad band characteristic of unprotonated 4VP H-bonded to SSA, which would most likely appear in this spectral area.

The nature of the equilibrium being affected by the change in temperature needs to be addressed if thermodynamic data are to be obtained from these spectra. It is well-known that carboxylic acids interact with alkylamines according to the following scheme:[27]

$$\text{A-H}\cdots\text{B} \rightleftharpoons \text{A}^-\ldots{}^+\text{H-B}$$

With the spectroscopic evidence at hand, we will tentatively assume a similar equilibrium is operative in the blends, governed by an equilibrium constant K_1:

$$\text{SSA}\cdots\text{4VP} \rightleftharpoons \text{SSA}^-\cdots\text{4VPH}^+ \quad K_1 = [\text{ion pair}]/[\text{SSA}\cdots\text{4VP}] \quad (1)$$

If the assumption is made that all 4VP units are either protonated or involved in the nonionic H-bonded pair, the expression for K_1 becomes

$$K_1 = p/(1-p) \quad (2)$$

van't Hoff plots of $\ln K_1$ versus $1/T$ were constructed from the IR/temperature data of the 5, 7, and 10% blends and are presented in Figure 10. Since molecular motions are essentially frozen-in below T_g, the dynamic equilibrium between the reactive species in the blend does not really exist at low temperatures. Indeed, the slope of a van't Hoff plot below T_g is usually much lower than that above T_g (see, for example, ref 28). Hence, the enthalpy change, $\Delta H°$, for the forward reaction indicated in eq 1 was evaluated from the slope of the high temperature portion ($T > T_g + 40$ deg) of the plots of Figure 10 using a least mean squares analysis; values of -13.5 ± 1.0, -16.0 ± 1.3, and -16.7 ± 0.5 kJ/mol were obtained for the 5, 7, and 10% blends, respectively.

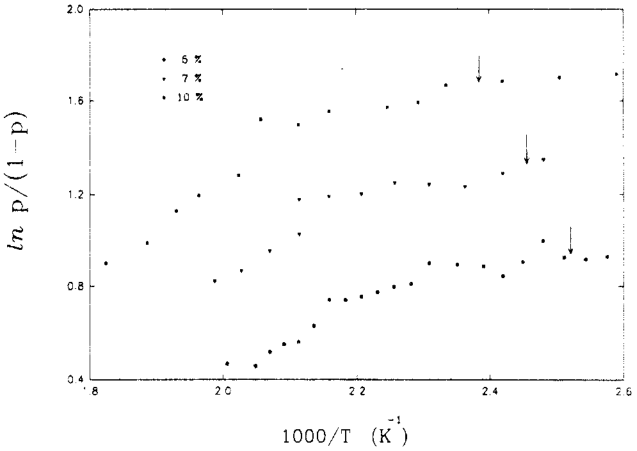

Figure 10. van't Hoff plots of the protonation–deprotonation equilibrium depicted in eq 1 for the 5, 7, and 10% blends. Arrows are located at the blend T_g's. Vertical shifts of 0.2 and 0.9 were introduced for the 7 and 10% blends, respectively.

For the sake of completeness, the spectroscopic data were interpreted as if the equilibrium present in the blend was similar to that presented in eq 1, with the difference that the un-ionized species are not H-bonded to each other:

$$\text{SSA} + \text{4VP} \rightleftharpoons \text{SSA}^-\cdots\text{4VPH}^+ \quad K_2 = [\text{ion pair}]/\{[\text{SSA}]\cdot[\text{4VP}]\} \quad (3)$$

For a given blend, it can be shown that K_2 is proportional to $p/(1-p)^2$. van't Hoff plots for the 5, 7, and 10% blends yielded values of $\Delta H°$ between −22 and −26 kJ/mol.

Both sets of values are much smaller than what one could reasonably expect for a proton transfer reaction involving a strong acid. Furthermore, the literature value for a very similar system, pyridine reacting in benzene with trichloroacetic acid[29] (a compound having a pK_a in water identical to that of SSA) is −57 kJ/mol, leading us to conclude that the equilibrium depicted in eq 3 is not a valid representation of what is occurring in the blends. The most logical interpretation of these results is that the equilibrium which is operative in these blends involves a H-bonded nonionic 4VP/SSA pair, as depicted in eq 1.

Consequences of Ionic Cross-Links on Mechanical Properties. An attempt will now be made to correlate the changes in the mechanical properties of the blends with functional group content. As spectroscopic evidence indicates, the pyridinium and sulfonate ions form an ion pair, i.e. an ionic cross-link. The introduction into a polymer of covalent cross-links is known to result in a decrease in free volume and a corresponding increase in T_g, as well as in the appearance of a stable post-T_g rubbery plateau in the modulus/temperature curves at modulus values significantly greater than 10^6 N/m^2. Earlier torsion pendulum studies have shown that the T_g of the blends increased with ion content and that the post-T_g modulus attained a value characteristic of entanglement coupling, i.e. of the order of 1×10^5 N/m^2 at $T_g + 40$ deg.[30] We will initially attempt to correlate the changes in the T_g of the blends with interacting group content and will subsequently present our interpretation of the absence of a post-T_g rubbery plateau.

Table 4. Experimental and Theoretical Values of T_g for the Series of Blends, Calculated Using DiBenedetto's and Nielsen's Equations, and Comparison with the Value of T_g Expected in the absence of Specific Interactions

% blend	X_c	T_{g_0} (°C)	$T_{g_{exp}}$ (°C)	$T_{g_{DB}}$ (°C)	T_{g_N} (°C)
2	0.020	103	112 ± 2	110	111
5	0.051	104	123 ± 2	124	123
7	0.070	105	132 ± 2	133	131
10	0.100	105	145 ± 2	147	143

Nielsen presented an equation derived theoretically by DiBenedetto relating the shift in T_g of a polymer following the introduction of cross-links:[31]

$$(T_g - T_{g_0})/T_{g_0} = KX_c/(1 - X_c) \qquad (4)$$

Here, X_c represents the mole fraction of the monomer units which are cross-linked while T_{g_0} is the hypothetical T_g of the polymer in the absence of cross-links and must take into account the copolymer effect of the cross-linking agent. The constant K, defined as the ratio of the lattice energies for cross-linked and un-cross-linked polymers, is said to be between 1.0 and 1.2. The theoretical treatment behind this equation was published recently.[32]

Assuming that all the acidic and basic groups have reacted to form ionic cross-links and that these would have the same effect on T_g as covalent cross-links, DiBenedetto's equation was used to calculate the theoretical T_g of each blend, $T_{g_{DB}}$, using a value for K of 1.0 and a value for X_c identical to the average functional comonomer content in the blend. The T_g of the blend in the absence of cross-links, T_{g_0}, was calculated using the Fox equation, which is also often used to calculate the T_g of copolymers:

$$1/T_{g_0} = w_1/T_{g_1} + w_2/T_{g_2}$$

where w_i and T_{g_i} refer to the weight fraction and T_g of component i in the blend. The T_g's of the blend components were obtained in the following fashion.

(1) S-SSA Component. The T_g of the S-SSA copolymer increases with SSA content mostly because of acid association in the polymer, which will be absent in the blend. Thus, using the T_g of the copolymer would erroneously increase the expected T_g of the blend. Consequently, the T_g of the S-SSA blend precursor was calculated using the Fox equation assuming the T_g of the SSA moiety to be the same as that of poly(4-*tert*-butylstyrene) (T_g = 127 °C[33]), for which the monomer has a flexibility and a volume resembling those of SSA.

(2) S-4VP Component. The T_g of the S-4VP series of copolymers was calculated using the Fox equation, with a T_g for P4VP of 142 °C.[33]

Table 4 presents the T_g's of the blends determined in the earlier study,[30] $T_{g_{exp}}$, together with the calculated values of T_{g_0} and $T_{g_{DB}}$. It is readily seen that the T_g's of the blends are within experimental error of the values predicted from DiBenedetto's equation when a value for K of 1.0 is used. Hence, it would appear that the ionic cross-links affect free volume exactly as would covalent cross-links, at least below T_g.

A similar conclusion was reached by using an empirical equation derived by Nielsen relating the change in T_g upon cross-linking:[31]

$$T_g - T_{g_0} = 3.9 \times 10^4/\bar{M}_c \qquad (5)$$

where $\bar{M}_c$ is the average molecular weight between cross-links. Assuming that $\bar{M}_c$ corresponds, in the present case, to the average molecular weight between neighboring SSA or 4VP units, values of T_g were calculated with eq 5 and are presented in Table 4 as T_{g_N}. These values are all within experimental error of $T_{g_{exp}}$. Previous studies have also shown that the increase in T_g with ion content of some ionomers can be predicted from equations derived for covalently cross-linked polymers.[34]

According to the classical kinetic theory of rubber elasticity,[35] the introduction of cross-links should also result in the appearance of a stable rubbery plateau characterized by an equilibrium shear modulus, G_E, at temperatures above T_g. The value of this modulus is given by

$$G_E = \rho RT/\bar{M}_c \qquad (6)$$

where ρ is the density of the polymer (1.04–1.065 g/cm^3 for PS[33]) and R is the ideal gas constant. Previous studies[30,36] indicate that the blends do not show an extended rubbery plateau above T_g, apart from that due to entanglement coupling at modulus values of approximately (1–2) × 10^5 N/m^2. If the ionic cross-links behaved as ideal cross-links, equilibrium shear moduli of 6, 17, 25, and 38 × 10^5 N/m^2 would be expected for the 2, 5, 7, and 10% blends, respectively, at T_g + 40 deg.

Hence, it can be concluded that the ionic cross-links are not permanent, i.e. that they yield within the time scale of the experiment, which was of the order of 10 s. This contrasts strongly with the results obtained by Otocka and Eirich on blends of butadiene–lithium methacrylate copolymers with butadiene–methyl-5-(2-methylvinyl)-pyridinium iodide copolymers, for which a rubbery plateau modulus at approximately 10^7 N/m^2 was observed up to the highest reported temperature of 75 °C.[37] The authors concluded that a small number of pyridinium carboxylate ion pairs had formed in these blends and acted like nonlabile cross-links. However, these two sets of observations are not contradictory because of the much lower T_g's of the blends of Otocka's study and the lower temperature range of the measurements performed.

Since the ionic cross-links are not permanent above T_g, they must interchange once large-scale segmental motion becomes possible. One plausible mechanism for this interchange could involve a pyridinium sulfonate ion pair reverting back to the nonionic form, as in eq 1, followed by diffusion of the neutral species. However, given the fact that many proton transfer reactions in water are so rapid that they are diffusion controlled, it may not be possible for the neutral species to separate in the very viscous polymer melt without the proton jumping back to the 4VP unit. A second plausible mechanism involves ion-hopping: the SSA$^-$ and 4VPH$^+$ units involved in a specific cross-link may separate long enough for chain slippage to occur, hopping along to form less strained cross-links with other 4VPH$^+$ and SSA$^-$ units. Ion-pair hopping has been postulated for flow processes in ionomers,[38] and a similar mechanism is possibly operative in the blends studied.

Conclusion

The blending of PS containing sulfonic acid functionality with PS containing 4VP units results in proton transfer from the acid to the base. Almost all of the 4VP units in the blends exist in the protonated form, H-bonded to the sulfonate ions. The effect of these ion pairs on the T_g of the polymer is identical to that of covalent cross-links. In contrast to these, however, the ion pairs do not increase the post-T_g modulus of the material and are thus thermally labile.

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