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Spectroscopic Study of an Ionic Blend Made from the Acid Form of Sulfonated Polystyrene and Poly[ethyl acrylate-*co*-(4-vinylpyridine)]

Kazuo Sakurai,[†] Elliot P. Douglas, and William J. MacKnight*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: Infrared spectroscopic measurements were performed for a series of stoichiometric blends made from sulfonated polystyrene and poly[ethyl acrylate-*co*-(4-vinylpyridine)]. Comparison of the spectra before and after blending revealed that the sulfonic acid groups formed sulfonate anions and the pyridine groups formed pyridinium cations in the blends. These changes were ascribed to an acid/base interaction occurring upon blending. Quantitative analysis in terms of both the S–O single-bond stretching and the pyridinium cation ring vibration band indicated that most of the sulfonic acid and pyridine groups took part in the interaction.

Introduction

The thermodynamic miscibility of two polymers requires a favorable polymer–polymer interaction, since the combinatorial entropy gain upon blending is too small to play a significant role in the free energy of mixing. Enhanced compatibility is expected for a blend modified so that an acid/base pair forms between the different polymer chains.[1-3] Eisenberg et al. have investigated intensively a series of such blends and have found that a critical modification level of 5% is necessary to induce miscibility as measured by dynamic mechanical techniques.[1] In our recent study[4] on the blend consisting of the acid form of sulfonated polystyrene (HSPS) and poly[ethyl acrylate-*co*-(4-vinylpyridine)] (EAVP), thermal and mechanical data indicate that such compatible blends are not miscible on the molecular level. The data suggest that micro-phase separation occurs in these blends even at a modification level of 10%. Our recent result illustrates the need for further study by use of a technique to probe these blends on a molecular level.

Fourier transform infrared spectroscopy (FTIR) is a powerful technique for investigating specific interactions in polymer blends.[5,6] This technique also provides a method for the estimation of the quantity of interactions which occur upon blending. In this paper, four blends made of HSPS and EAVP with modification levels ranging from 0 to 10% are examined by FTIR.

Experimental Section

Three blends with different modification levels were made by mixing tetrahydrofuran solutions of HSPS and EAVP. The sulfonation level of HSPS was 1.7, 5.7, and 7.6 mol %, and the pyridine content in EAVP was 2.4, 5.2, and 10.6 mol %. Each blend was prepared so as to contain stoichiometric amounts of sulfonate and pyridine groups from EAVP and HSPS with similar functional group contents. As a reference, a blend was made from polystyrene (PS) and poly(ethyl acrylate) (EA). The details for the sample preparation and blending procedure have been described previously.[4] Table I summarizes the nomenclature of the blends studied in this paper, along with molecular weights and functional group contents for each individual polymer.

Transparent and clear films of 5–10-μm thickness were made by compression molding PS, HSPS, and the blends. The procedure was to press the sample at 175 °C for 6 min under vacuum. For the compression die, two flat aluminum plates covered by a Teflon-coated aluminum foil was used. The coated surface made it easy to peel off the sample and gave a smooth surface to the film. The technique of molding an IR-transmitting disk using KBr powder was not suitable for HSPS because cationic exchange takes place in the molded disk, causing undesirable peak shifts. All EAVP samples were prepared by solvent casting a film from tetrahydrofuran–EAVP solution directly on a KBr transmitting window. The spectra were checked carefully to ensure that the KBr did not cause any apreciable peak shifts in the EAVP films.

Five nonstoichiometric blends were made to estimate the extinction coefficient for a characteristic pyridinium cation peak in the blend. Compression-molded films were made for HSPS-rich samples according to the method mentioned above, and for EAVP-rich blends the casting technique on the KBr window was adopted.

Infrared absorption was measured using an IBM IR/32 FT-IR spectrometer at a resolution of 2 cm^{-1} averaged over 30 scans. Before the measurement, each sample was dried for a few hours at 70 °C under vacuum.

Results and Discussion

(1) IR Spectra and Peak Assignment. Figure 1 shows absorption spectra measured for 5HSPS, 8HSPS, and PS from 500 to 1400 cm^{-1}. In this region, sulfonate groups exhibit characteristic bands. Comparing the spectra shows that there are six new peaks in 5HSPS and 8HSPS at 580, 906, 1009, 1100, 1176, and 1350 cm^{-1} and that they become more intense with increasing sulfonation level. According to Detoni and Hadzi's spectroscopic study[7] of aromatic sulfonic acids, the two strong bands at 1350 and 1176 cm^{-1} can be assigned to the symmetric and antisymmetric stretching of S═O═S, respectively. A relatively broad band around 900 cm^{-1}, which overlaps a polystyrene band at 906 cm^{-1}, is due to S–O stretching. Furthermore, an angle deformation vibration of S═O═S can be ascribed to a shoulder appearing at the higher wavenumber side of a polystyrene peak at 550 cm^{-1}. A relatively small band at 1100 cm^{-1} is due to the first overtone of the angle deformation. Table II summarizes the assignments of the new peaks of HSPS along with EAVP.

All new peaks discussed above are ascribed to sulfonic acid vibrations. It should be noted that there is no trace of either hydrated sulfonate acid or sulfonate anion, which are expected to exhibit peaks around 1140 and 1200 cm^{-1} from symmetric and antisymmetric stretching, respectively.

[†] Permanent address: Research & Development Center, Kanebo Ltd., 1-5-90 Tomobuchi-cho, Miyakojima-ku, Osaka, Japan.

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Table I
Nomenclature of Blends and Characteristics of Individual Polymers

	sulfonated polystyrene			poly[ethyl acrylate-*co*-(4-vinylpyridine)]		
blend		sulfonation level, mol %	$10^{-3}M_w$		pyridine content, mol %	$10^{-3}M_2$
00	PS	0	250	EA	0	890
2H2	2HSPS	1.7	250	2EAVP	2.4	730
5H5	5HSPS	5.7	250	5EAVP	5.2	406
8H10	8HSPS	7.6	250	10EAVP	10.6	315

Table II
Assignment of New Peaks in HSPS and EAVP

	peak position, cm^{-1}	assignment	peak descrip
HSPS	580	S=O=S angle def	weak, shoulder
HSPS	907[a]	S-O str	medium, broad, overlap
HSPS	1009[a]	ring vib of *p*-substituted benzene ring	very weak, shoulder
HSPS	1100[a]	overtone of S=O=S angle def	weak
HSPS	1176[a]	S=O=S str, sym	strong, sharp
HSPS	1350[a]	S=O=S str, antisym	strong, broad
EAVP	1402[a]	ring vib of pyridine	medium

[a] Disappearing peak upon blending.

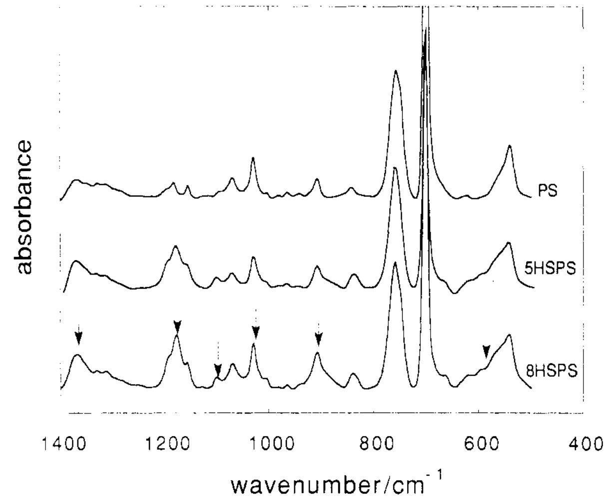

Figure 1. IR absorption spectra of PS (upper curve), 5HSPS (middle), and 8HSPS (lower) in the 500–1400-cm^{-1} range; the arrows show new peaks in HSPS.

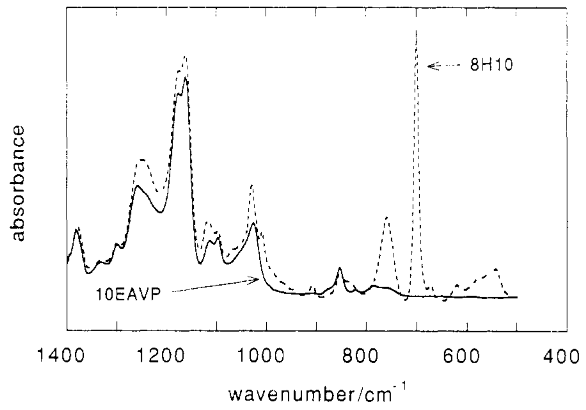

Figure 2. Comparison of spectra of 8H10 (broken line) and 10EAVP (solid line) in the 500–1400-cm^{-1} range.

The presence of a band from the OH bond in the sulfonic acid should be mentioned. The OH stretching vibration is reported to appear usually as a broad band near 2900 cm^{-1}. In comparison with PS, all HSPS samples show a relatively small shoulder at the higher wavenumber side of the CH stretching band at 2930 cm^{-1}. This shoulder could be assigned to the OH stretching of the sulfonic acid.

Figure 2 shows spectra for 8H10 and 10EAVP in the same region as discussed in Figure 1. In the spectrum of the blend the bands from both 10EAVP and 8HSPS overlap with each other and form a relatively complicated spectrum. To define the changes in the sulfonic acid bands in the blend, the spectrum of 10EAVP was subtracted from that of 8H10. The subtraction was done by minimizing the area of the carbonyl stretching peak at 1734 cm^{-1} in the subtracted spectrum, so that all peaks in the resultant spectrum are due to either 8HSPS or interactions upon blending. The resultant spectrum is shown in Figure 3, denoted as 8H10–10EAVP, along with that of 8HSPS. Comparing these spectra, it is clear that the blend exhibits new peaks at 1009, 1117, and 1248 cm^{-1}. On the contrary, the S-O stretching around 900 cm^{-1} and the O=S=O stretching at both 1176 and 1350 cm^{-1} decrease or disappear in the blend. Referring to a previous assignment for hydrated aromatic sulfonic acids,[8] these new peaks can be described in the following way. The prominent strong band at 1248 cm^{-1} and the band at 1117 cm^{-1} are attributed to the antisymmetric and symmetric stretching of the delocalized sulfonate anion (SO_3^-), respectively, and the peak at 1009 cm^{-1} is assigned to the disubstituted benzene ring deformation. Table III summarizes these assignments. The changes in the spectra upon blending indicate that the sulfonic acid converts to sulfonate anion upon blending.

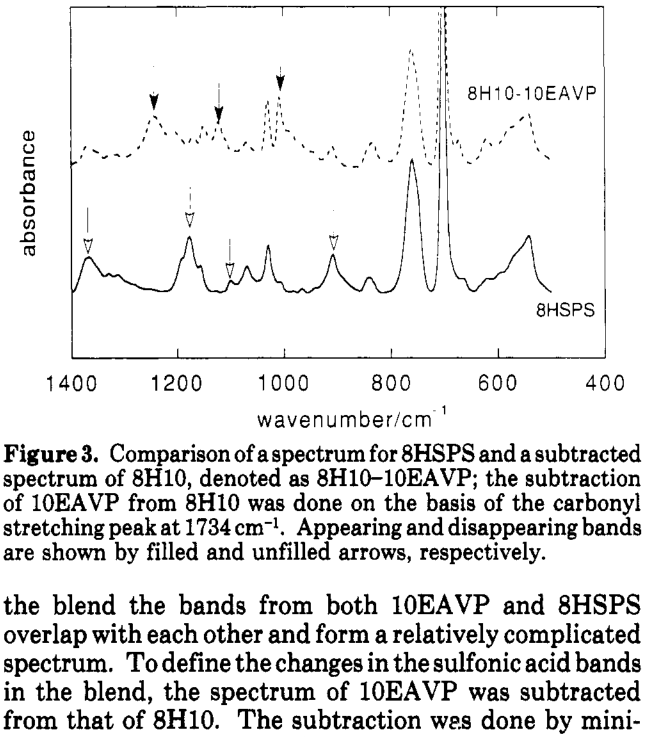

Figure 3. Comparison of a spectrum for 8HSPS and a subtracted spectrum of 8H10, denoted as 8H10–10EAVP; the subtraction of 10EAVP from 8H10 was done on the basis of the carbonyl stretching peak at 1734 cm^{-1}. Appearing and disappearing bands are shown by filled and unfilled arrows, respectively.

A notable feature observed in the spectra for the blends is that peak splitting due to a decrease in molecular symmetry does not occur in the sulfonate anion antisymmetric stretching vibration at 1248 cm^{-1}. This fact suggests

Table III
Assignment of New Peaks in the Acid Blend

peak position, cm^{-1}	assignment	peak descrip
1009	ring vib of *p*-substituted benzene ring	medium, shoulder
1117	SO_3^- str, sym	medium, overlap
1248	SO_3^- str, antisym	strong, broad overlap
1638	ring vib of pyridinium cation	medium

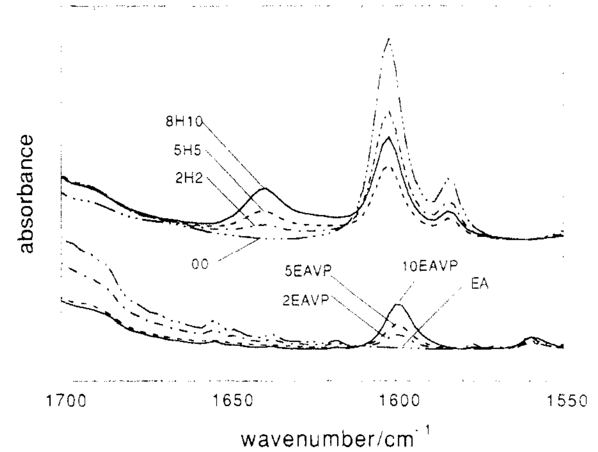

Figure 4. IR absorption spectra for the pyridine ring stretching band at 1602 cm^{-1} in EAVP and the pyridinium cation band at 1638 cm^{-1} in the blends.

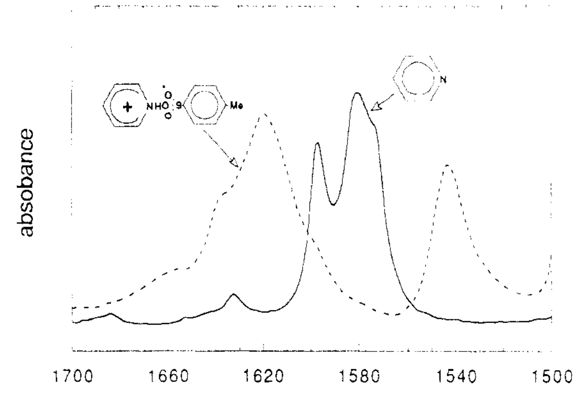

Figure 5. Comparison of spectra for pyridine and a pyridinium complex made from pyridine and *p*-toluenesulfonic acid from 1700 to 1500 cm^{-1}.

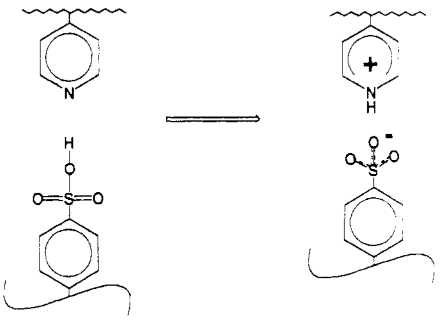

Figure 6. Schematic diagram for the interaction mechanism of EAVP and HSPS.

that the proton has completely transferred from sulfonic acid to pyridine, so that the three S–O bonds are equivalent.

This proton transfer explains the emergence of the peak at 1009 cm^{-1} due to the disubstituted benzene ring in the following way. When the proton is transferred from the SO_3H group to the pyridine group, the remaining sulfonate anion becomes an electron donor and therefore increases the electron density on the sulfonated benzene ring. The higher electron density on the benzene ring causes the position of the peak to shift to lower wavenumbers compared to HSPS. In fact, this band is well-known to be strongly affected by substitution.[6,9] The original peak for disubstituted benzene which should exist in HSPS might be obscured by a strong band from PS at 1027 cm^{-1}.

Figure 4 shows spectra for a series of EAVP and the blends in the range 1700–1550 cm^{-1}. Each EAVP copolymer exhibits an isolated band at 1602 cm^{-1} which becomes stronger with increasing pyridine content. This peak can be assigned to the ring-stretching mode for the 4-substituted pyridine group.[8] The blends exhibit three bands at 1638, 1600, and 1570 cm^{-1}. Comparing them with the reference spectra of the unfunctionalized blend (00) and EA, the 1570- and 1600-cm^{-1} bands seem to arise from PS, but the 1638-cm^{-1} band has no counterpart in either PS or EA. The appearance of this new band at 1638 cm^{-1} must therefore be attributed to proton transfer from the sulfonic acid to the pyridine group upon blending.

It is common practice to use model compounds to assign unknown bands. A pyridinium complex made of *p*-toluenesulfonic acid and pyridine can be reasonably regarded as a model compound for the interacting groups between HSPS and EAVP. Figure 5 compares spectra for pyridine and the stoichiometric pyridinium complex. The spectrum for pyridine has two peaks around 1600 cm^{-1}, and each peak can be assigned to an in-plane ring vibration of pyridine.[8] Upon formation of the complex, the positions of these pyridine peaks merge together and shift to higher wavenumbers. The shift can be explained by a reduced electron density on the pyridinium cation which results from proton transfer between pyridine and sulfonic acid.

By analogy with the model compound, the peak at 1638 cm^{-1} in the blend can be assigned to a ring-stretching vibration of the pyridinium cation which interacts with the sulfonic acid. It should be noted that the 1638-cm^{-1} peak is as sharp as the original pyridine peak and there is no substantial peak between them. This fact suggests the absence of an interaction consisting of an intermediate state between pyridine and the pyridinium cation. This feature is clearly consistent with the lack of splitting in the antisymmetric stretching band of the sulfonate anion. Therefore it can be confirmed that the interaction mechanism is an acid/base pair rather than hydrogen bonding. The interaction mechanism is illustrated schematically in Figure 6.

The spectra of 8H10 and 5H5 show a rather broad band from N–H stretching in the range from 2400 to 2800 cm^{-1}. This fact also confirms the occurrence of proton transfer to the pyridine.

(2) Quantitative Analysis. To estimate to what extent the acid/base pair interactions take place upon blending, quantitative analysis was done based on both the S–O stretching peak at 906 cm^{-1} and the characteristic pyridinium peak at 1638 cm^{-1}. These peaks are relatively isolated so that errors from arbitrary base line corrections are expected to have little effect on the result.

Figures 7 and 8 show a series of spectra for HSPS and the blends in the 750–1000-cm^{-1} region. These spectra demonstrate the dependence of the S–O stretching intensity on the degree of sulfonation. The peak intensity for HSPS at 906 cm^{-1} increases with increasing sulfonation level. On the contrary, the peaks for all the blends seem to be the same shape as for PS. This feature is seen more clearly in Figure 9. In this figure, the area of each peak at 906 cm^{-1} is normalized based on a PS peak at 759

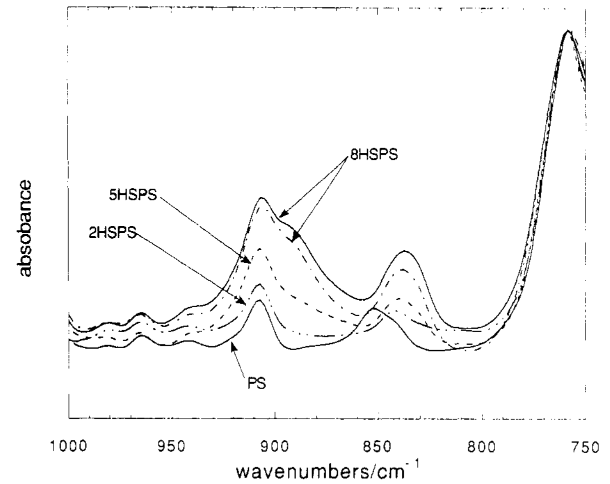

Figure 7. Comparison of the spectra of the S–O single bond stretching vibration between HSPS and PS.

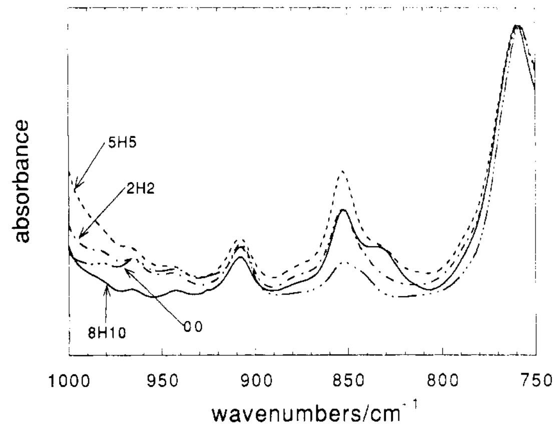

Figure 8. Comparison of the spectra of the S–O single bond stretching vibration among the blends.

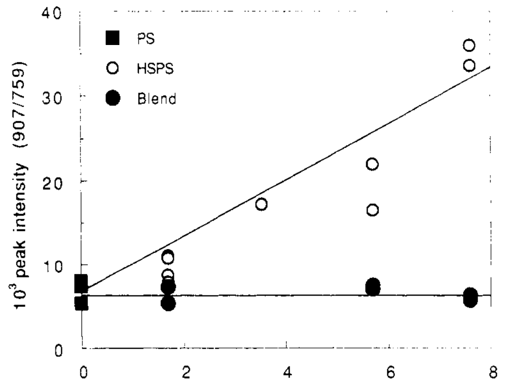

Figure 9. Sulfonation level dependence of the peak area at 906 cm^{-1} for HSPS and the blends; the area is normalized on the basis of a polystyrene peak area at 759 cm^{-1}.

cm^{-1} and plotted against sulfonation level. The data points for HSPS increase linearly with increasing sulfonation level. However, the blends show no increase in the area of the S–O band. These data suggest that all the sulfonic acid groups present transfer a proton to the pyridine in the blend.

The data points in Figure 9 are relatively scattered due to experimental error. Some of these errors might be due to sample preparation; others could arise from the base line corrections. The magnitude of the errors in Figure 9 can be estimated to be ±3 in the normalized area. For a 2% sulfonation level this error is comparable to the difference between 2HSPS and 2H2. At this sulfonation level, therefore, it is not possible to state with certainty whether proton transfer is complete or not. However, for 8H10 and 5H5, the difference is large enough to conclude that most, if not all, of the sulfonic acid groups are involved in the interaction.

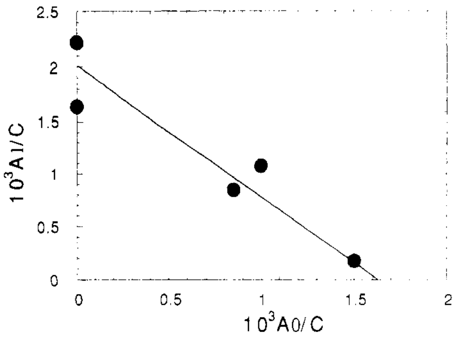

Figure 10. Estimation of extinction coefficients according to eq 2 using nonstoichiometric blends.

As mentioned in the previous section, a vibration mode for the pyridine ring in EAVP appears at 1602 cm^{-1} as an isolated peak. After blending, the polystyrene portion of HSPS has two large peaks at the same position. The intensities of these peaks are almost 10 times as large as that of pyridine even in 8H10. Therefore, they might obscure the pyridine peak, even if some pyridine groups do not take part in the interaction. This situation makes it difficult to compare the peak intensity between pyridine and the pyridinium cation in the blend. However, the intensity of the pyridine peak can be made comparable to the polystyrene peak in the EAVP-rich nonstoichiometric blends. For these blends, the subtraction of PS from the blend can reveal an appreciable pyridine peak. Using these blends, an extinction coefficient for the pyridinium cation can be evaluated in the following way.

The extinction coefficients for pyridinium cation and pyridine are related to the peak areas of both bands by the following equation:

$$A_0/\alpha + A_1/\beta = C \qquad (1)$$

Here, A_0 is the normalized peak area for pyridine, α is the extinction coefficient for A_0, A_1 is the normalized peak area for pyridinium cation, β is the extinction coefficient for A_1, and C is the pyridine content in EAVP. This equation is valid for all copolymer compositions regardless of the extent to which pyridines interact in the blend and is also applicable to nonstoichiometric blends. It depends solely on the validity of the Lambert–Beer law. Rearrangement of eq 1 gives

$$\frac{A_1}{C} = \beta - \frac{\beta}{\alpha}\frac{A_0}{C} \qquad (2)$$

This equation indicates that A_1/C plotted against A_0/C should give a straight line whose slope is $-\beta/\alpha$ and intercept is β. Therefore, by determining the slope and the intercept both extinction coefficients can be estimated experimentally from eq 2.

Three nonstoichiometric blends with pyridine/sulfonic acid molar ratios of 0.9, 0.75, and 0.20 were made from 8HSPS and 10EAVP. Two blends with ratios of 0.75 and 0.20 were made from 5HSPS and 5EAVP. The subtraction of the PS spectrum from these blend spectra was done based on a PS peak at 759 cm^{-1}. Figure 10 shows a plot of A_1/C against A_0/C for the nonstoichiometric blends. Here, a carbonyl stretching peak at 1734 cm^{-1} is used for the normalization. From the slope and the intercept, the extinction coefficient of the pyridinium cation can be estimated to be 2.3–1.8 × 10^{-3} mol $\%^{-1}$.

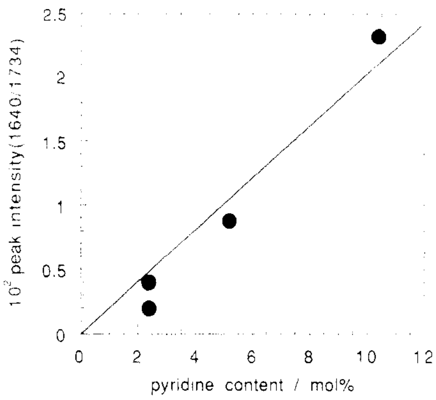

Figure 11. Comparison of experimental data and the calculation (β = 0.002) for the area of the pyridinium cation peak.

Assuming all pyridines take part in the interaction, the peak area for the pyridinium cation can be calculated for a given blend by use of the extinction coefficient and the pyridine content. Figure 11 illustrates the result of this calculation shown as a solid line ($\beta = 2 \times 10^{-3}$). The figure also shows data obtained for the stoichiometric blends as circles. The agreement between the calculation and experiment shows that most of the pyridines react to form pyridinium cations upon blending. It is noted that the area of the pyridinium cation peak for 2H2 is not large enough for accurate quantitative analysis.

These results are consistent with the quantitative analysis of the S–O stretching vibration discussed earlier. For 5H5 and 8H10, it can be concluded that most sulfonic acids in HSPS transfer a proton to the pyridines in EAVP upon blending to make the acid/base ion pair, and there are few noninteracting pyridines or sulfonic acids left in the blend.

(3) Position of the Carbonyl Stretching Band. In the series of studies for this ionic blend, the same sample has been investigated by use of dynamic mechanical analysis, differential scanning calorimetry, and optical microscopy. The results show that some phase separation occurs even in 8H10, and the domain size is much smaller than the spatial resolution of the dynamic mechanical measurement.[4] It is also demonstrated that a micro-phase-separated morphology[10] is consistent with the experimental data for the blend.[4]

Coleman and Painter have studied extensively infrared spectroscopy for a wide range of miscible and immiscible polymer blends.[5] According to their study of a blend made from poly[ethylene-*co*-(vinyl acetate)] (EVA) and poly(vinyl chloride), the carbonyl band in EVA shifts 5 cm^{-1} lower in a miscible blend compared to an immiscible blend. This shift is significant and can be explained by a change in environment surrounding the carbonyl group upon blending.

Figure 12 compares the carbonyl peaks of 5EAVP, 10EAVP, 5H5, and 8H10. These four peaks have the same breadth and position. It suggests that the local environment of the EAVP chain might not be perturbed upon blending. This result is consistent with the presence of micro-phase separation in this blend.[4]

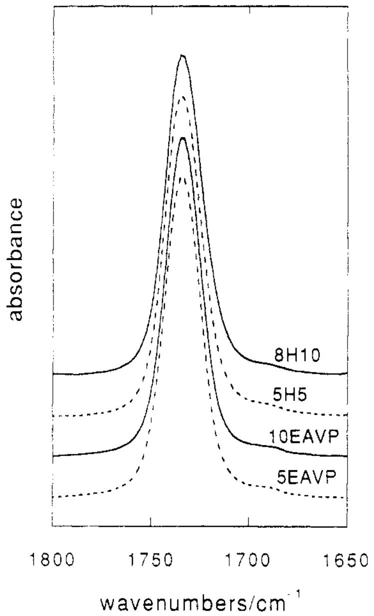

Figure 12. Comparison of the carbonyl peak for 5EAVP, 10EAVP, 5H5, and 8H10.

Conclusions

IR spectroscopic measurements reveal that proton transfer from sulfonic acid to pyridine takes place upon blending HSPS and EAVP. For 5H5 and 8H10, most of the functional groups interact with each other. Coincidence in the position of the carbonyl stretching band between EAVP and the blends suggests that micro-phase separation occurs in the blend.

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Registry No. EAVP (copolymer), 28963-65-7.