Spectroscopic Study of Zinc Neutralized Sulfonated Polystyrenes and Blends with Poly[ethyl acrylate-*co*-(4-vinylpyridine)]

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

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

Received July 7, 1992; Revised Manuscript Received September 10, 1992

ABSTRACT: Infrared spectroscopic studies were carried out on hydrated and dehydrated forms of zinc neutralized sulfonated polystyrenes (ZSPS) and their stoichiometric blends with poly[ethyl acrylate-*co*-(4-vinylpyridine)] (EAVP). Dehydrated ZSPS shows an intense peak from the antisymmetric stretching band of the sulfonate group, and hydration causes this band to broaden and diminish. At saturation of hydration ZSPS absorbs three water molecules per sulfonate group, which is equivalent to the number of the coordinated water molecules in zinc hexahydrated *p*-toluenesulfonate. Blending shows the same effect as the dehydration making the antisymmetric stretching band more intense and sharper. Furthermore the water band around 3500 cm^{-1} disappears upon blending. These facts lead to the conclusion that the pyridine group takes the place of the water and coordinates to the zinc in the blend.

Introduction

Compatibility is expected for a blend modified so that an attractive ionic interaction forms between the different polymer chains.[1-3] Eisenberg et al. have investigated intensively a series of such blends and confirmed that specific interactions considerably enhanced compatibility between two polymer chains that were otherwise completely immiscible. Recently we have studied an ionic blend consisting of sulfonated polystyrene and poly[ethyl acrylate-*co*-(4-vinylpyridine)] (EAVP).[4,5] Our thermal and mechanical data[4] indicate that such ionic blends are microphase separated rather than miscible on the molecular level. We thus refer to them as compatible. The subsequent study[5] by FTIR reveals that most of the functional groups are involved in the interaction for the blend made from the acid form of sulfonated polystyrene and EAVP. This spectroscopic study also confirms the model[4,6] that the topological constraint imposed by the interaction leads to the microphase separation in those types of blends.

Peiffer et al. proposed a coordination interaction mechanism for the blend made from metal neutralized sulfonated ionomers and pyridine copolymers.[7] However, little has been done to study the interaction mechanism for such types of blends. In this paper we will report the results of a spectroscopic study of zinc neutralized sulfonated polystyrenes (ZSPS) and their blends with EAVP and also will interpret spectral changes upon blending using the model of the coordination interaction.

Experiment

The samples of ZSPS were kindly provided by EXXON Research and Engineering Co. and the copolymers of EAVP were synthesized by free radical polymerization in methanol.[4] Sulfonation levels of ZSPS and pyridine contents in EAVP are given in Table I along with molecular weights and nomenclatures used in this study.

Three stoichiometric blends with different modification levels were made from EAVP and ZSPS with similar functional group contents. The ZSPS and EAVP were dissolved separately in dimethylformamide at a concentration of about 1%. The solution of EAVP was added to the ZSPS solution dropwise over a period of about 1 min while stirring. After adding the EAVP solution the mixture became turbid due to formation of a gel. After completion of mixing, the gel was isolated from the solvent by precipitating into a large amount of water. The resultant gel was dried at 60 °C for 3 days under vacuum.

Table I
Nomenclature of Blends and Characteristics of Individual Polymers

	zinc sulfonate polystyrene			poly[ethyl acrylate-*co*-(4-vinylpyridine)]		
blend sample		sulfonation level, mol %	mol wt $10^{-3}M_w$		pyridine content, mol %	mol wt $10^{-3}M_w$
2Z2	2ZSPS	2.1	250	2EAVP	2.4	730
5Z5	5ZSPS	5.5	250	5EAVP	5.2	406
7Z10	7ZSPS	7.3	250	10EAVP	10.6	315

The films for IR spectroscopic measurement were made by compression molding for ZSPS and the blends[5] and by solvent casting on a KBr window from THF for the EAVP's. After the films were dried at 70 °C for 1 day in vacuum, IR absorption was measured using an IBM IR/32 FT-IR spectrometer averaged over 30 scans and at a resolution of 2 cm^{-1}.

It should be mentioned that the drying temperature significantly affected the amount of residual water in ZSPS. When 7ZSPS was dried at 100 °C for 3 days under vacuum, most of the water seemed to be eliminated. The dried film appeared slightly brown in color, suggesting that degradation took place during the treatment. On the other hand drying at 70 °C did not cause any appreciable change in color but some amount of water still remained in the sample as shown in the next section. In the case of the hydration–dehydration experiment mentioned below, we first dried the sample at 100 °C to eliminate residual water as much as possible. In all other experiments we adopted the drying condition of 70 °C for 1 day under vacuum to avoid substantial changes in the IR spectrum.

A film of 7ZSPS weighing about 1 g was dehydrated at 100 °C for 3 days under vacuum and then hydrated by suspending over water in a closed desiccator at 25 °C. After an appropriate time, the film was taken out of the desiccator and dried for 5 min in a vial with silica gel at the bottom in order to take out extra water absorbed on the surface of the film. After the measurement of weight increase and IR spectra, the film was suspended again in the humid atmosphere in the desiccator and the hydration was continued.

Results and Discussion

(1) Spectra for ZSPS. Figure 1 compares spectra for ZSPS, PS, and HSPS (sulfonated polystyrene acid form) in the range from 500 to 1500 cm^{-1} where aromatic sulfonate compounds are expected to have characteristic bands. As reported in our previous paper,[5] the sulfonate group in

---

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

0024-9297/93/2226-0208$04.00/0

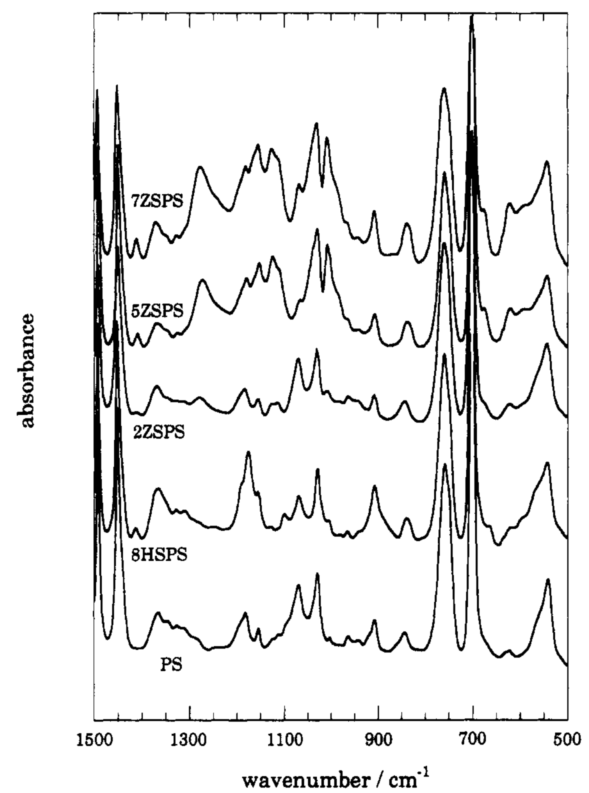

Figure 1. Comparison of spectra of PS, HSPS, and ZSPS in the range of 500–1500 cm^{-1}.

HSPS shows characteristic bands corresponding to the S=O bond and the S—O bond; 907 cm^{-1} for the S—O stretching mode and 1176 and 1350 cm^{-1} for the O=S=O symmetric and antisymmetric stretching mode, respectively. On the other hand ZSPS shows a quite different and more complicated spectrum than that of HSPS. Peaks at 1002 and 1270 cm^{-1} and the shoulders around 1044 cm^{-1} become prominent with increasing sulfonation level in ZSPS. Furthermore a broad band appears around 1100–1200 cm^{-1} which overlaps the peaks of polystyrene.

Para-substituted benzene rings in polystyrene are expected to have an in-plane vibration mode for the benzene ring at 1013 ± 7 cm^{-1}.[8,9] This vibration interacts with the stretching of the bond attached to the 3 carbon in the phenyl ring and gives rise to a substituent-sensitive band. The sharp peak at 1002 cm^{-1} can be assigned to the in-plane vibration of the benzene ring as reported by Fitzgerald and Weiss.[9] However peak overlap in this region makes it difficult to give a certain assignment for the other peaks. Either a shoulder around 1040 cm^{-1} or a broad band between 1100 and 1200 cm^{-1} might be assigned to symmetric stretching of SO_3^-. On the other hand either a sharp peak at 1270 cm^{-1} or one of the bands between 1100 and 1200 cm^{-1} might be due to the antisymmetric stretching mode of SO_3^-. It is also possible that one of the peaks between 1100 and 1200 cm^{-1} is due to in-plane stretching of the para-substituted benzene ring. In fact the assignment for this region is still a question under debate.[9]

It is well-known that metal neutralized sulfonate ionomers have some water in the cluster even after substantial drying and a significant spectral change in the range 1000–1300 cm^{-1} results from the water. Zundel[10] examined the effect of hydration on the IR spectra for fully sulfonated polystyrene neutralized with various transition metals. His data show that dehydration causes a drastic change in the band for the antisymmetric stretching of sulfonate anion around 1200 cm^{-1}. This change is significant and illustrates the necessity of taking account of any water which might be interacting with the sulfonate group in ZSPS.

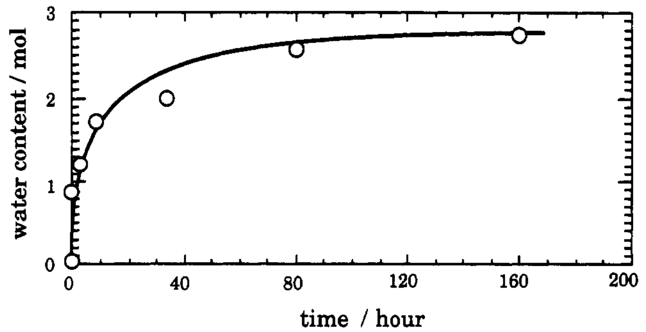

Figure 2. Plot of amount of absorbed water per sulfonate group in 7ZSPS against exposed time to a humid atmosphere.

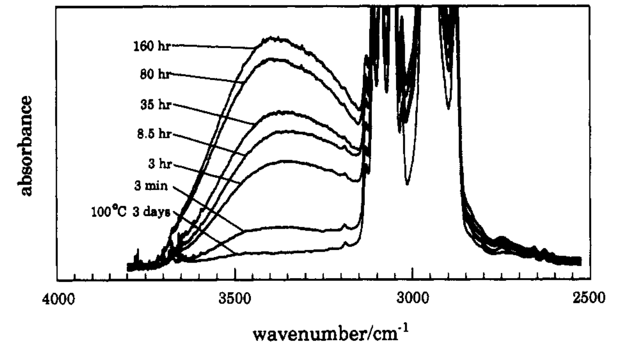

Figure 3. Spectral changes in the water band around 3400 cm^{-1} observed for 7ZSPS in the water absorption process. Each spectrum corresponds to a data point in Figure 2.

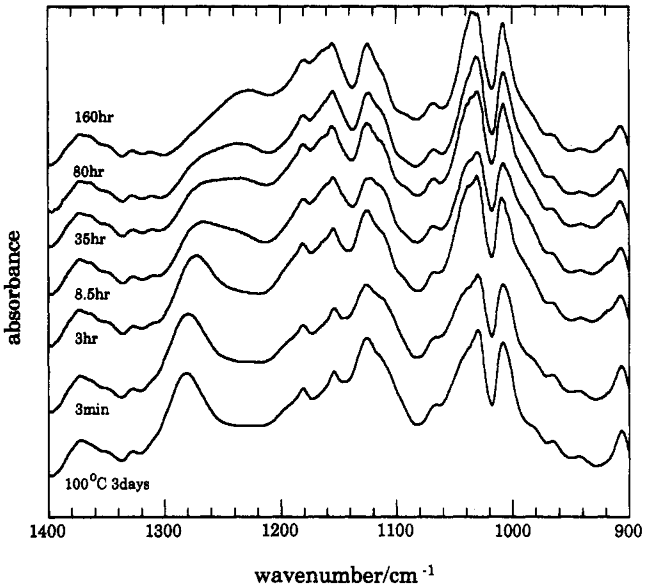

Figure 4. Spectral changes in the sulfonate band in the range 1400–900 cm^{-1} observed for 7ZSPS in the water absorption process. Each spectrum corresponds to a data point in Figure 2.

Figure 2 plots the amount of absorbed water by 7ZSPS per sulfonate group against the time exposed to a humid atmosphere. The absorption seems to reach saturation after 100 h and each sulfonate group contains three water molecules in the fully hydrated state. Figures 3 and 4 show the IR spectra corresponding to each data point in Figure 2. Upon hydration the characteristic band for water around 3000–4000 cm^{-1} becomes dominant as shown in Figure 3 and a substantial spectral change in the sulfonate group band takes place in the range of 1400–900 cm^{-1} as shown in Figure 4. The hydration of 7ZSPS also causes

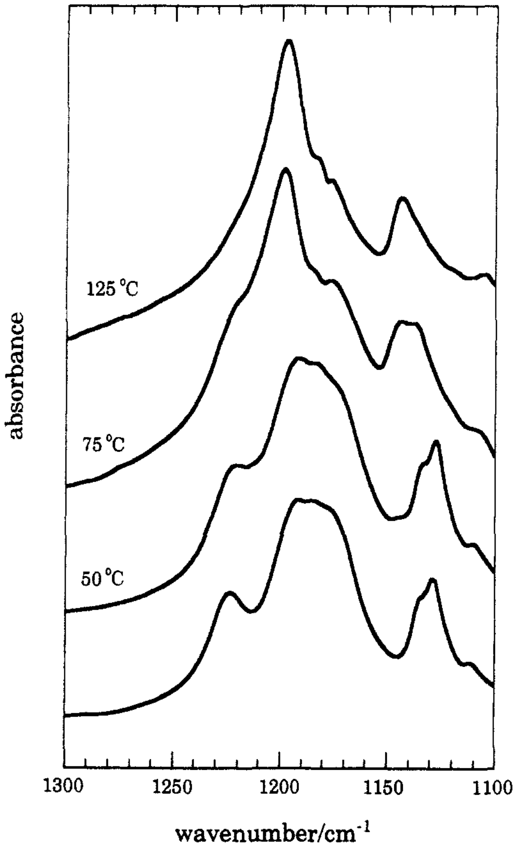

Figure 5. Change in the antisymmetric vibration peak in PTSZ upon dehydration.

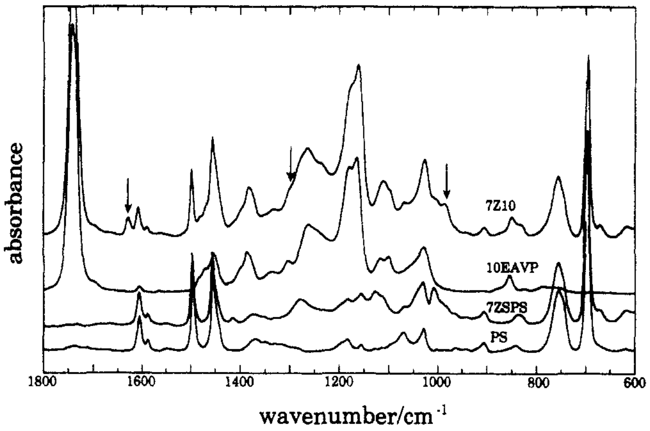

Figure 6. Comparison of the spectra for 7Z10, 10EAVP, 7ZSPS, and PS. Peaks induced by blending are shown by arrows.

a major change observed around 1270 cm^{-1}. As the water content increases, the sharp band at 1270 cm^{-1} tends to broaden and diminish and a new broad band appears around 1210 cm^{-1}. Being referred to Zundel's study,[10] the peak at 1270 cm^{-1} may be assigned to the antisymmetric stretching of SO_3^-.

Zinc hexahydrated *p*-toluenesulfonate (PTSZ) is a reasonable model compound for the ionic multiplet in ZSPS. Figure 5 demonstrates the dehydration effect on the IR spectra for the model compound. Hydrated PTSZ has a strong band at 1190 cm^{-1} which is assigned to the antisymmetric stretching of SO_3^-. With increasing drying temperature the antisymmetric stretching band tends to split and finally a sharp peak appears at the higher wavenumber side of the antisymmetric band. This change in the spectrum of PTSZ coincides with the change in the spectrum around 1270 cm^{-1} of 7ZSPS in the hydration process described above. This confirms that the band at 1270 cm^{-1} in dehydrated 7ZSPS is due to the antisymmetric stretching of SO_3^-. As mentioned later, a water molecule is considered to bind to the sulfonate group in ZSPS by hydrogen bonding. Consequently, the shift of the 1270 cm^{-1} band to lower wavenumbers with the hydration of ZSPS may be attributed to the change in polarization of the SO_3^- by the formation of hydrogen bonds between water and the sulfonate group.

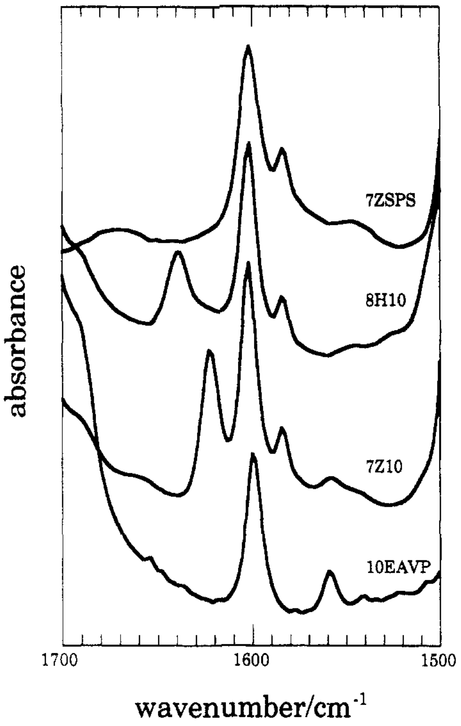

Figure 7. IR absorption spectra for the pyridine ring stretching band at 1602 cm^{-1} in 10EAVP and the pyridinium cation band at 1638 cm^{-1} in the blends.

A crystallographic study[11] revealed that fully hydrated PTZS has six water molecules. Each water is bound to the oxygen atom of the sulfonate group by hydrogen bonding, and at the same time the water molecules coordinate to the zinc ion as a ligand. It should be noted that the number of water molecules absorbed by 7ZSPS at saturation is three per sulfonate group, which is the same number of water molecules as in hydrated PTZS. This coincidence suggests that the water molecule in the multiplet of ZSPS is present as a ligand of the zinc ion rather than as free water. A thermal study[12] by TGA and DTA showed that four of the six waters can be easily removed by heating and that the last two waters can remain bound up to 100 °C because of the hydrogen bonding with the sulfonate group. This fact also coincides with the difficulty of removing water from ZSPS. The above discussion leads to the speculation that the sulfonate group of ZSPS traps some water in the multiplet and at the same time the water coordinates to the zinc atom as a ligand. However a confirmation of this speculation is needed by Raman and far-infrared spectroscopic studies or a heavy water absorption experiment.

(2) Spectra for the Blend. Figure 6 shows a comparison of the spectrum in the range from 600 to 1800 cm^{-1} for 7Z10 with those of two individual polymers, 10EAVP, 7ZSPS, and PS. Here the spectra are normalized in terms of either a carbonyl stretching band at 1734 cm^{-1} or a polystyrene band at 700 cm^{-1}. Comparing the spectra shows that blending produces a new peak at 1621 cm^{-1} and a shoulder around 980 cm^{-1}. However, overlapping in the range between 1000 and 1400 cm^{-1} makes it difficult to identify the changes in the sulfonate group which might occur upon blending.

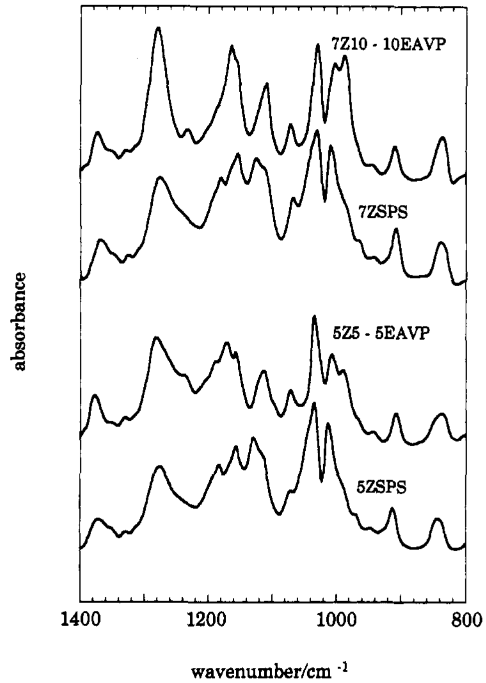

Figure 8. Comparison of spectra for 7ZSPS and 5ZSPS with subtracted spectra of 7Z10 and 5Z5 denoted as 7Z10–10EAVP and 5ZSPS–5EAVP, respectively; the subtraction was done based on the carbonyl stretching peak at 1734 cm^{-1}.

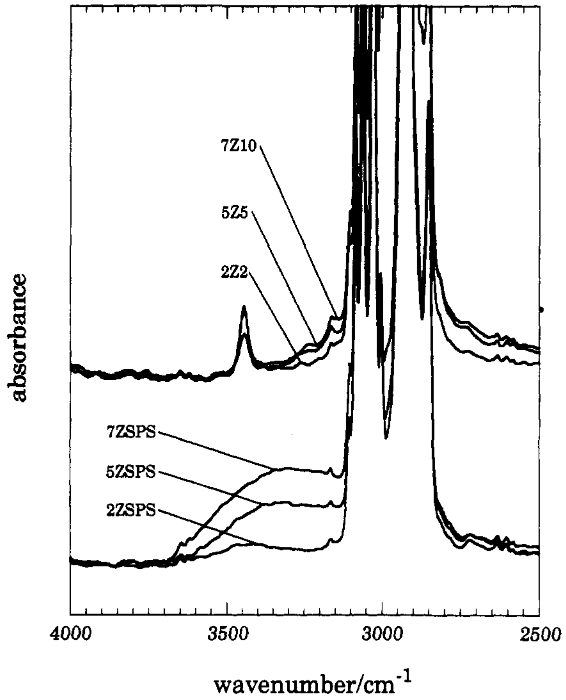

Figure 9. Comparison of spectra between ZSPS and the blends in the water band region 2500–4000 cm^{-1}.

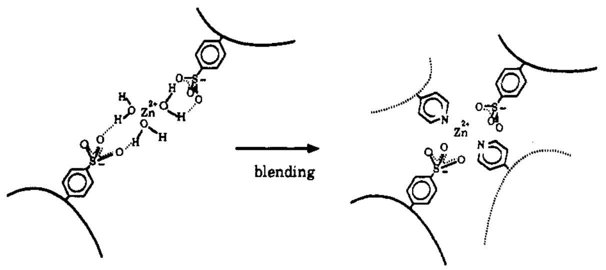

Figure 10. Schematic model for the coordination interaction for the blend made from ZSPS and EAVP.

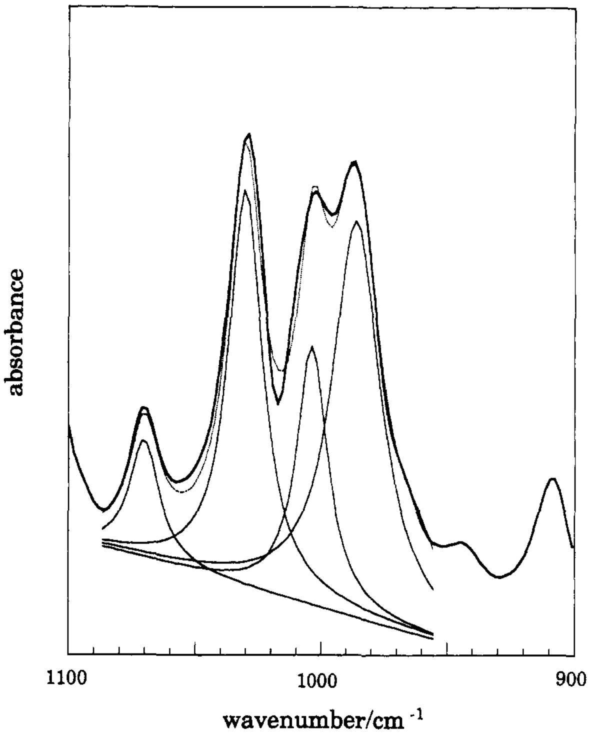

Figure 11. An example of a deconvolution in the range from 950 to 1090 cm^{-1} for the spectrum of 7Z10–10EAVP.

The region around 1600 cm^{-1} is magnified in Figure 7 and the spectrum of 7Z10 is compared with 8H10 (acid blend; see ref 5), 7ZSPS, and 10EAVP. As reported in our previous paper,[5] the peak at 1621 cm^{-1} in the blend can be assigned to a stretching vibration mode for the positively charged pyridinium ring, the same assignment as the peak at 1638 cm^{-1} in the acid blend. These peaks have the same vibration mode as the peak at 1600 cm^{-1} in 10EAVP and are considered to result from a shift to higher wavenumbers due to an interaction between the sulfonate group and the pyridine ring. The peak in the acid blend shifts more than that of 7Z10. The difference in the amount of the shift of 20 cm^{-1} can be attributed to the fact that acid/base pairs have a stronger interaction than ion-pair/ion interactions.

As mentioned before, the change in peaks between 1000 and 1400 cm^{-1} is not easy to distinguish due to overlapping. In order to define the change of the sulfonate group bands in the blend, the spectra of 10EAVP and 5EAVP were subtracted from those of 7Z10 and 5Z5, respectively. 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 ZSPS or interactions upon blending. The resultant spectra are shown in Figure 8, denoted as 7Z10-10EAVP and 5Z5–5EAVP. Also shown are those of 7ZSPS and 5ZSPS. Upon blending, the antisymmetric stretching of SO_3^- at 1270 cm^{-1} becomes sharper and more intense and also a new peak appears at 983 cm^{-1}. Furthermore a peak around 1160 cm^{-1} increases and a peak around 1120 cm^{-1} decreases.

As shown in Figure 4, when ZSPS is hydrated, the antisymmetric stretching band of SO_3^- at 1270 cm^{-1} becomes weaker in the early stage of the hydration. On the other hand, Figure 8 illustrates that the antisymmetric band becomes larger by blending, which is a reverse process of the early stage of the hydration. This fact suggests that blending causes elimination of the waters which are coordinated to the zinc ion in ZSPS. The elimination of the water upon blending is confirmed by the change of a characteristic band for water around 3000–3500 cm^{-1} as

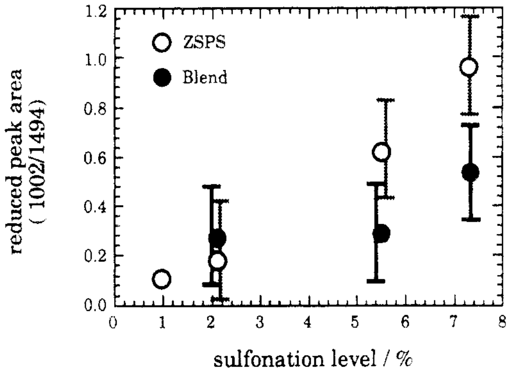

Figure 12. Sulfonation level dependence of the peak area at 1002 cm^{-1} for ZSPS and the blends; the area is normalized based on a polystyrene peak area at 1494 cm^{-1}.

illustrated in Figure 9. After blending there is no appreciable band due to water. This is a distinctive effect of blending, taking account of the fact that water bonded to ZSPS is hard to dry out completely. In comparison with Figures 2 and 3, the amount of water in ZSPS after the standard drying condition of 70 °C for 1 day is roughly estimated to be 1 molecule per sulfonate group, or 2 molecules per zinc. These waters are considered to coordinate to the zinc and at the same time bond to the sulfonate group by hydrogen bonding. Since pyridine is a ligand which can interact more favorably with zinc than water, pyridine can take the place of water upon blending as illustrated schematically in Figure 10. This model for the interaction can explain the elimination of water which causes the enhanced intensity of the antisymmetric stretching band for the sulfonate group.

As shown in Figure 8, blending causes a new peak to appear at 983 cm^{-1} and the peak at 1002 cm^{-1} to decrease compared to the spectra of ZSPS. Since the peak at 1002 cm^{-1} is a substituent-sensitive band of in-plane vibration for the benzene ring,[9] the peak at 983 cm^{-1} is considered to result from a shift of the peak at 1002 cm^{-1} due to the interaction. In other words, the peaks at 1002 and 983 cm^{-1} can be assigned to an interacting band and noninteracting band, respectively. The extent of the shift due to interaction seems to be large, but the reason for such a large shift is not clear.

The spectrum in the region from 950 to 1090 cm^{-1} was deconvoluted into four bands by assuming a combination of Gaussian and Lorentzian functions. In order to decrease the number of adjustable parameters, the peak positions were fixed for all bands. An example of this curve fitting analysis is shown in Figure 11. Since the peak at 1028 cm^{-1} is from polystyrene, the validity of this analysis can be confirmed by comparing the resultant peak area at 1028 cm^{-1} in the blend with the area of that band in polystyrene. Figure 12 plots normalized peak area of the noninteracting peak as a function of sulfonation level of ZSPS and blends. Despite the fact that there are rather large experimental errors, it can be concluded that some sulfonate groups remain noninteracting.

If some sulfonate groups are not involved in the interaction, these noninteracting ionic pairs can still keep water as a ligand. As mentioned before in Figure 9, however, no trace of the water band is observed in the range of 3000–3600 cm^{-1} in the blends. The reason for this discrepancy is not clear. One possible explanation is that when we made the blend by solution mixing, all sulfonate groups might react with pyridines and all water bonded to the zinc might be substituted by the pyridine. To make a thin film for IR measurement, we had to mold the blend at 175 °C under vacuum for a few minutes and quenched to room temperature. This molding temperature is higher than the ionic cluster transition temperature.[13] Therefore we might expect that interactions can be broken by the molding and some of them cannot reform due to fast cooling.

It should be mentioned that blending also causes the peak around 1160 cm^{-1} to increase and the peak around 1120 cm^{-1} to decrease as shown in Figure 8. Unfortunately the assignment for these peaks is not clear. There were no corresponding peaks observed for a model complex made from pyridine and hydrated zinc *p*-toluenesulfonate. A possible explanation for these peaks is that they are due to the vibrational coupling between different sulfonate groups within an ionic cluster.[14] Raman and far-infrared spectroscopic study can give further information about ionic cluster and the change of the clusters upon blending.

Acknowledgment. The authors thank Dr. Dennis G. Peiffer and Dr. Robert D. Lundberg of Exxon Research and Engineering Company for providing the sulfonated polystyrenes, GPC analysis, and many helpful discussions. K.S. thanks Kanebo Ltd. for providing him the opportunity to work on this project. Funding was kindly provided by U.S. Army Grant DAAL03-91-G-0127. Acknowledgment is made to the UMASS Material Research Laboratory, funded by the National Foundation for support through the use of the central facilities.

References and Notes

(1) Smith, P.; Hara, M.; Eisenberg, A. *Current Topics in Polymer Science Volume II*; Ottenbrite, R. M., Ed.; Hanser Publishers: Munich, Vienna, New York, 1987; p 256.
(2) Smith, P.; Eisenberg, A. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 223.
(3) Eisenberg, A.; Smith, P.; Zhou, Z. L. *Polym. Eng. Sci.* **1982**, *22*, 1117.
(4) Douglas, E. P.; Sakurai, K.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 6776.
(5) Sakurai, K.; Douglas, E. P.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4506.
(6) Brereton, M. G.; Vilgis, T. A. *Macromolecules* **1990**, *23*, 2044.
(7) Peiffer, D. G.; Hager, B. L.; Weiss, R. A.; Agarwal, P. K.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1869.
(8) Colthup, N. B.; Doly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1990.
(9) Fitzgerald, J. J.; Weiss, R. A. *Coulombic Interactions in Macromolecular Systems*; American Chemical Society: Washington, DC, 1986; p 35.
(10) Zundel, G. *J. Membr. Sci.* **1982**, *11*, 249.
(11) Gunn, A. F.; Scott, R. A. *Nature* **1946**, *158*, 620.
(12) Bombin, M.; et al. *Thermochim. Acta* **1989**, *146*, 341.
(13) Douglas, E. P.; Sakurai, K.; MacKnight, W. J. To be submitted for publication in *Macromolecules*.
(14) Ishioka, T. Doctoral Thesis, Osaka University, 1990.

Registry No. EAVP, 28963-65-7.