Organomet. Chem., **228**, 223 (1982).
22. J. Otera, T. Yano and K. Kusakabe, *Bull. Chem. Soc. Jpn.*, **56**, 1057 (1983).
23. T. P. Lockart, W. F. Manders, E. O. Schlemper and J. J. Zuckerman, *J. Am. Chem. Soc.*, **108**, 4074 (1986).
24. R. Okawara and M. Wada, *Adv. Organomet. Chem.*, **5**, 137 (1967).
25. W. F. Edgell and C. F. Ward, *J. Mol. Spect.*, **8**, 343 (1962).
26. T. N. Srivastava and V. Kumar, *J. Organomet. Chem.*, **107**, 55 (1976).
27. M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, **30**, 3231 (1968).
28. A. G. Davies, P. G. Harrison, J. D. Kennedy, T. N. Mitchell, R. J. Puddephatt and W. McFarlane, *J. Chem. Soc.* (C), 1136 (1969).
29. J. C. May, D. Petridis and C. Curran, *Inorg. Chim. Acta*, **5**, 511 (1971).

Spectral and Thermal Studies of Transition Metal PSSA Ionomers

Il Wun Shim*

Department of Chemistry, Chung-Ang University, Seoul 156-756

William M. Risen, Jr.

Department of Chemistry, Brown University, U.S.A. *Received July 4, 1988*

Transition metal PSSA ionomers containing Co(II), Ni(II), Cr(III) Ru(III), and Rh(III) are investigated by IR,Far-IR, UV-Vis and DSC. Reliable IR Spectroscopic criteria are established for assessing the degree of ion-exchange of PSSA ionomers and the local structures around metal cations in them. In the hydrated transition metal PSSA ionomers, the ionic groups are solvated by water molecules and there is no significant interactions between sulfonate group and metal cations. The visible spectra indicated that metal cations are present as $[M(H_2O)_6]^{n+}$ with Oh symmetry. Their T_g values increase as the extent of ionic site concentraion increases, but there is no direct dependence of T_g on the nature of metal cations or their oxidation states. Thus, the water content in PSSA ionomer is found to have dominant influence on T_g of hydrated transition metal PSSA ionomers. Dehydration of the hydrated transition metal PSSA ionomers results in direct interaction between ionic groups and significant color changes of the ionomers due to the changes of the local structures around metal cations. On the base of spectral data, their local structures are discussed. In case of dehydrated 12.8 and 15.8 mol % transition metal PSSA ionomers, no glass transtion is observed in 25-250 °C region and this is believed to arise from the formation of highly cross-linked structures caused by direct coordination of sulfonate groups of metal cations. In the 6.9 mol % transition metal PSSA ionomers, the glass transition is always observed whether they are hydrated or dehydrated and this is though to be caused by the sufficient segmental mobility of the polymer backbone.

Introduction

Ionomers are a relatively new class of amorphous materials based on organic polymers that are functionalized with ionic groups such as SO_3^- or COO.$^-$[1-5] These materials have been under intensive study in recent years because of their potential applications such as gas separation materials, heterogeneous catalytic supports and solid state ionic electrolytes for use in batteries.[6-10]

Sulfonated linear polystyrene(PSSA) which is among the typical ionomers was developed by Lundberg and coworkers at EXXON[11,12] and related research on these PSSA ionomers has been focused on the questions of whether ionic domains form, what structures exist in them, how they depend on ionic site concentrations or on the nature of cations and how their properties, especially, their glass transition temperatures vary with cations, anionic site concentrations and thermal history. In 1984, Mattera and Risen carried out a series of systemic spectroscopic studies and reported the dependence of properties of the PSSA ionomers on the ionic site concentrations and the nature of the metal cations in alkali and alkaline earth metal PSSA ionomers, in which cation site attractions are coulombic in nature.[13] Also, some interesting catalytic reactivity of rhodium and ruthenium metals, contained within the ionic domain of PFSA and PSSA ionomers, was reported recently.[14,15,16]

However, there has been no reports about the study of the metal site interactions and the effect of transition metal on the thermal property of transition metal PSSA ionomers, which is believed to be important for the development of ionomer supported catalyst system.

In this background, several PSSA ionomers containing Co (II), Ni(II), Cr(III), Ru(III), and Rh(III) ions at different ionic site concentration have been investigated by various spectroscopic methods and the differential scanning calorimetry. The results are reported in this paper.

Experiments

The sulfonated linear polystyrene(PSSA) ionomers were kindly provided by Dr. R.D. Lundberg of the EXXON Research and Engineering Co. who developed the materials.[17] Their chemical composition can be represented as follows:

1

where the value of $a = y/(x + y)$ represents the mole fraction of sulfonate ionic groups. The sulfonate compositions (mole percent = a × 100) employed in this study are 6.9%, 12.8%, and 15.8%. The average spacings between the sulfonated styrene groups and the neutralization equivalent weights can be represented as below:

mole % of PSSA	spacings	neutralization eq. weights
6.9 %	14	1500
12.8 %	8	800
15.8 %	6	700

Transparent thin films were prepared to *ca.* 20μm thickness, which is convenient for study by transmission IR spectroscopy, by dissolving the H^+ forms in tetrahydrofuran and casting on glass plate. After the solvent evaporated at room temperature, the films were rinsed with distilled water and dried at 110 °C in vacuum for two days to remove any THF solvent from the films.

Ion-exchange procedure:

Method A. Various transition metal ions were incorporated by ion-exchange process in which the PSSA films were stirred in flasks which contain 0.06 M aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$(Mallinckrodt Chem. Works), $RuCl_3 \cdot 1\text{-}3H_2O$(Afla Products), $Co(NO_3)_2 \cdot 6H_2O$(Allied Chem.), and $RhCl_3$·Hydrate (Engelhard) for two weeks at room temperature. The films which became colored upon ion-exchange were removed from the solutions, rinsed with distilled water and allowed to dry in air. These films are designated in the form A% PSSA-M(B) where A gives the ionic site concentration (mol %), M and B designate various transition metals and their oxidation states.

Method B. Another ion-exchange procedure was employed in order to obtain complete ion-exchange on some 6.9% PSSA ionomers, since these were found not to be ion-exchanged completely by method A. Thus, about 2g of 6.9% PSSA dissolved in 30 m*l* THF was added dropwise to aqueous solutions containing 0.06 M Co(II), and Ni(II). Then each gum like polymeric material was taken out of the solution, rinsed with distilled water and allowed to dry in air at room temperature. Some portions of these materials were dissolved in boiling THF, and finally thin films of ion-exchange ionomers (6.9%) were made by evaporating the THF solvent slowly at room temperature. After this desolvation treatment, the films containing Co(II) and Ni(II) ions became colored pale pink and pale green, respectively. Those films are found to be completely ion-exchanged by IR spectroscopy.

Spectroscopic method. The IR spectra of air dried, ion-exchanged films in the 3800-400 cm^{-1} region were recorded at room temperature with a Digilab 15B FT-IR spectrometer at 2 cm^{-1} resolution and Nicolet MX-S FT-IR.

For the IR spectra of dried, ion-exchanged films, the specially designed reactor/IR cell was used.[16]

Far-IR spectra of the films in the 500-50 cm^{-1} region were recorded with Digilab 14 spectrometer, and each trace represents the average of at least 400 scans recorded with 4 cm^{-1} resolution. For the Far-IR spectra of dried samples, the ionomer films, which were dehydrated in the reactor cell at 110 °C in vacuum for 2 days, were taken out of the cell in glove box and put between two polyethylene windows, and the windows were sealed to protect the film from the hydration in air.

The UV-Vis absorption spectra in the 900-190 nm region were measured on a Perkin-Elmer 552A spectrometer. For dried samples, the ionomer films that had been used for IR spectra in their dehydrated condition were used immediately after taking them out of the cell under the nitrogen.

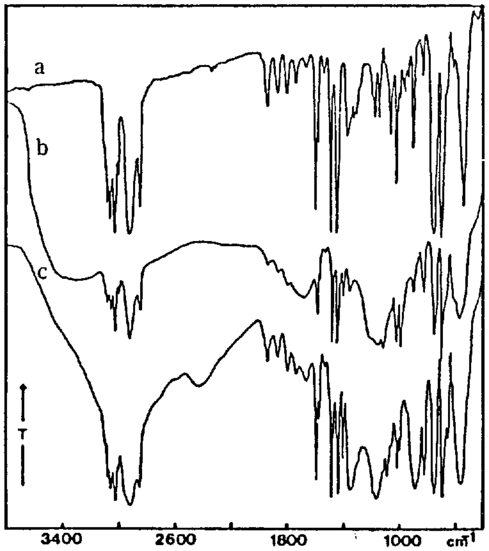


Figure 1. Infrared spectra of (a) polystyrene, (b) hydrated 15.8% PSSA-H film, and (c) dehydrated 15.8% PSSA-H film(neat).

Differential scanning calorimetry. A series of measurements of the glass transition temperature (Tg) were carried out using a Perkin-Elmer Model DSC-2 and Dupon Model 910 Thermal analyzer, whose sampling area was enclosed in a glove box under nitrogen. In a typical DSC scan sequence, dg/dt was measured on heating at 20 °C/min from 25 °C to an upper limit of 220 °C. It was held at that temperature for 10 min and then quenched to 25 °C at 320 °C/min and the second thermogram was obtained on heating at 20 °C/min from 25 °C to 220 °C. Further several DSC scans were made on the cycles of heating at the same conditions and automatically quenching at 320 °C/min to 25 °C or annealing at −10 °C/min.

In order to ascertain the effects of hydration and dehydration in transition metal ionomers on their thermal behavior, two other sets of experiments were carried out. In one, hydrated (air dried) specimens of ionomers were sealed mechanically in aluminum pans that had a small hole in the lid so that the ionomer samples could be dehydrated by heating them in the DSC instrument in which the sampling area was continuously purged with dry nitrogen. In the other, hydrated ionomer samples were encapsulated in aluminum pans with small hole as above, and they were dried in vacuum at 110 °C for two days before the DSC measurement were made. Both of these types of samples were thermally investigated by the same methods given above.

Results and Discussion

Infrared spectral study of PSSA ionomers

A. IR spectra of PSSA-H ionomers. In order to interpret various IR spectra of transition metal PSSA ionomers, the IR spectra of pure PSSA ionomers (PSSA-H) at different ionic site concentration of 6.9%, 12.8%, and 15.8% were obtained in hydrated and dehydrated conditions (Figure 1 and Table 1). They include many of the same bands that are char-

Table 1. Characteristic Infrared Spectral Data of PSSA-H Ionomers (cm^{-1})

[a]Hydrated PSSA-H Ionomer	[b]Dehydrated PSSA-H Ionomer	Assignments
3400(br)	—	OH stret. vib. of hydrated H_2O.
—	2950	OH stret. vib. of sulfonate groups.
—	2440	First overtone of OH bending vib.
1635(br)	—	H_2O scissor vib.
—	1350	S = 0 stret. vib., antisymmetric
1200(sh)	—	SO_3^- stret. vib., antisymmetric
—	1172	S = 0 stret. vib., symmetric
1128	—	In-plane skeleton vib. of benzene ring with SO_3^- substituents.
—	1101	In-plane skeleton vib. of benzene ring with SO_3H substituents.
1034(sh)	—	SO_3^- stret. vib., symmetric
—	1019,1011	In-plane C-H bending of benzene ring with SO_3H substituents.
1005	—	In-plane C-H bending of benzene ring with SO_3^- substituents.
—	900(sh)	S-O stret. vib.
669	664	C-S stret. vib.

[a] Dried at room temperature in air. [b] Dried at 110 °C in vacuum for 2 days. sh; shoulder, br; broad.

acteristics of polystyrene in their intensities and positions which were analyzed by Liang and Krimm.[18] In hydrated case, two strong broad bands at 3400 and 1635 cm^{-1}, arising from the hydrated water molecules in the sulfonate ionic domains, were observed and their intensities increase as ionic site concentration does. But, detailed analysis was difficult due to the strong features.

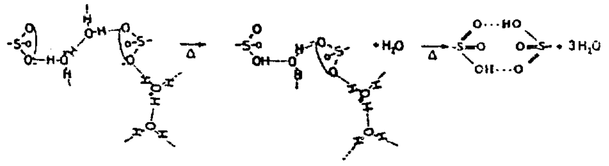
In the case of dehydrated PSSA-H ionomer films (dried at 110 °C in vacuum for 2 days), the spectra were well defined and there were new bands due to the presence of sulfonate groups at 2950(sh), 2440, 1415, 1350, 1172, 1101, 1019, 1011, 900(sh), and 664 cm^{-1}, which were quite similar to those of polyelectrolytic PSSA and a variety of its metallated forms, analyzed by G. Zundel.[19] The polyelectrolytic PSSA materials differ importantly from ionomeric PSSA used in this study. Their polymer backbone are covalently crosslinked with divinyl benzene, and they typically do not form ionic domains.[3-5] They are insoluble in organic solvents, and in some case, every styrene group is sulfonated. But their IR spectra were helpful to interpret various IR spectra of PSSA ionomers in this research.

The intensities of the bands due to the sulfonte groups are found to increase as the ionic site concentration does. However, the intensity and the band width variation with the ionic site concentration are not simple, because the tendency to form domains and the perturbation to the polymer backbone also vary with the ionic site concentrations.

According to Zundel's analysis, the bands at 2950(sh) and 2440 cm^{-1} can be assigned to the O-H stretching vibration of hydrogen bridged sulfonate groups and the first overtone of OH bending vibration, respectively. The band at 1415 cm^{-1}, which is absent from the spectrum of polystyrene, is assigned to one of the skeletal stretching vibrations of the benzene rings with a sulfonate substituent and this is confirmed by isotopic comparison.[19]

The vibrational modes due to the RSO_3^- groups in the hydrated PSSA ionomers can be predicted on the basis of the C_{3v} point group. When the three S-O bonds are equivalent with C_{3v} symmetry, two IR active modes are expected, an A mode (symmetric stretch, Vs) and a doubly degenerate E mode (asymmetric stretch, Va). Thus, the two bands at 1200 (sh) and 1034 cm^{-1} are assigned to $\nu a(SO_3^-)$ and $\nu s(SO_3^-)$, respectively.

When the PSSA-H ionomer films are dehydrated throughly, these bands disappear and three new bands at 1350(sh), 1172, 900(sh) cm^{-1} are observed and this can be explaned from the fact that, if the degeneracy is removed, the νs and νa bands are expected to split into several bands for different modes of vibration resulting from the lowered symmetry. Accordingly, the two bands at 1350 and 1172 cm^{-1} can be assigned to asymmetric and symmetric stretching vibration of SO bonds with double bond character, respectively. The band at 900(sh) cm^{-1} is assigned to the stretching vibration of the SO bond with single bond character. These changes can be seen in following schematic representation of dehydration process:



Other bands, observed at 1101(1128 in hydrated PSSA), 1011, and 664 cm^{-1} are easily assigned to in-plane skeletal vibrations of benzene ring with strong participation of the substituents, in-plane C-H bending vibration of benzen ring, and C-S stretching vibration, respectively since these are well characterized by Zundel[19] and Kresze *et al.*[20] (the bands at 1101 and 1011 cm^{-1} are found to depend on the degree of hydration).

The band at 1019 cm^{-1} was not reported by Zundel, but it is assigned to an in-plane C-H bending vibration of the benzene rings with SO_3H substituents, since this band appears only in thoroughly dried PSSA ionomers, and its intensity increases as the ionic site concentration increases. Also, it disappears in the IR spectra of transition metal PSSA ionomers. This study provided useful spectroscopic criteria for the IR spectral study of transition metal PSSA ionomers, especially estimating the degree of ion-exchange of PSSA ionomers.

B. IR spectra of hydrated transition metal PSSA ionomers. In the IR spectra of transition metal PSSA ionomers containing Co(II), Ni(II), or Cr(III), the bands due to the $-SO_3H$ substituents at 2950, 2440, 1350, 1172, and 900(sh) cm^{-1} disappear completely, showing that all of the sulfonate groups are neutralized as expected. In the case of PSSA ionomers containing Ru(III) and Rh(III), the intensities of the bands decrease significantly, but they do not disappear, which indicate that the ion-exchange is not complete in those cases. The elemental analysis of Ru containing ionomers showed that about 75% of the sulfonate groups in the 16.8% PSSA ionomers were neutralized.[15] The reasons for such incomplete ion-exchange in Ru(III) or Rh(III) containing ionomers are not clear, but it is believed that $RuCl_3$ or $RhCl_3$ hydrolize incompletely in aqueous solutions and there are some constraints on placing three SO_3^{-1} groups next to tripositive

Table 2. Infrared Spectral Data for Hydrated Transition Metal PSSA Ionomers (cm^{-1})

[a]Co(II)	Ni(II)	Cr(III)	Ru(III)	Rh(III)	[b]Assignments
3375	3300	3400	3400	3400	OH-stret. vib. of H_2O
1630	1640	1640	1640	1640	H_2O scissor vib.
1120	1210	1210	1210	1200	$\nu a(SO_3^-)$
1128	1126	1128	1125	1128	In-plane skeleton vib. of benzene ring with SO_3^- substituents.
1036	1037	1035	1034	1034	$\nu s(SO_3^-)$
1009	1009	1009	1008	1009	In-plane C-H bending of benzene ring with SO_3^- substituents.
675	680	675	675	675	ν(C-S)

[a]PSSA-Co(II), PSSA-Ni(II), PSSA-Cr(III), PSSA-Ru(III) and PSSA-Rh(III). [b]See Table 1.

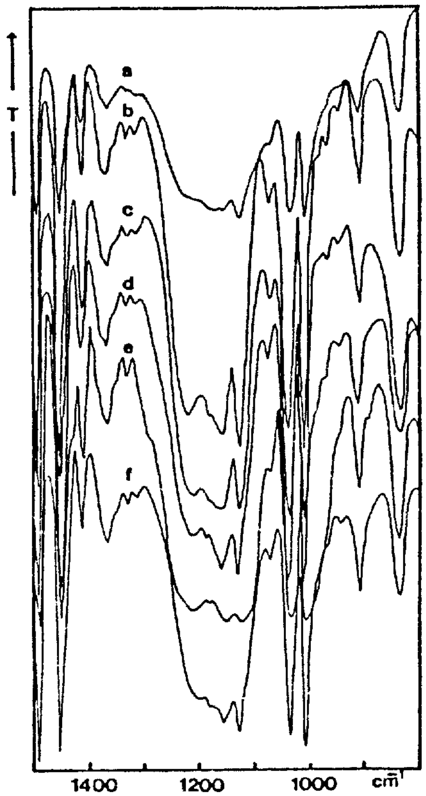


Figure 2. Infrared spectra of hydrated transition metal ionomers in the 1500-800 cm^{-1} region: (a) 15.8% PSSA-H, (b) 15.8% PSSA-Co (II), (c) 15.8% PSSA-Ni(II), (d) 15.8% PSSA-Cr(III), (e) 15.8% PSSA-Ru(III), (f) 15.8% PSSA-Rh(III).

Ru(III) or Rh(III) ions.

The hydrated transition metal ionomers, containing Co (II), Ni(II), Cr(III), Ru(III), and Rh(III), show quite similar IR spectra, regardless of the metal cations and their oxidation states as summarized in Table 2 and Figure 2. In their typical spectra, there are several bands at 3400, 1640, 1210, 1128, 1035, 1009, and 680 cm^{-1} which do not belong to polystyrene backbone. These are quite similar to the characteristic bands of hydrated PSSA-H ionomers, which suggests that both hydrated ionomers have similar structures (see Table 1 and 2). Thus, the bands are assigned in the manner as discussed in the spectra of the hydrated PSSA-H ionomers and the assignments are listed in Table 2. This result indicates that, when the transition metal PSSA ionomers are hydrated, there is no appreciable direct interaction between the sulfonate groups and the hydrated transition metal cations and the sulfonate groups, solvated mostly by water molecules, retain the C_{3v} symmetry as in hydrated PSSA-H ionomers.

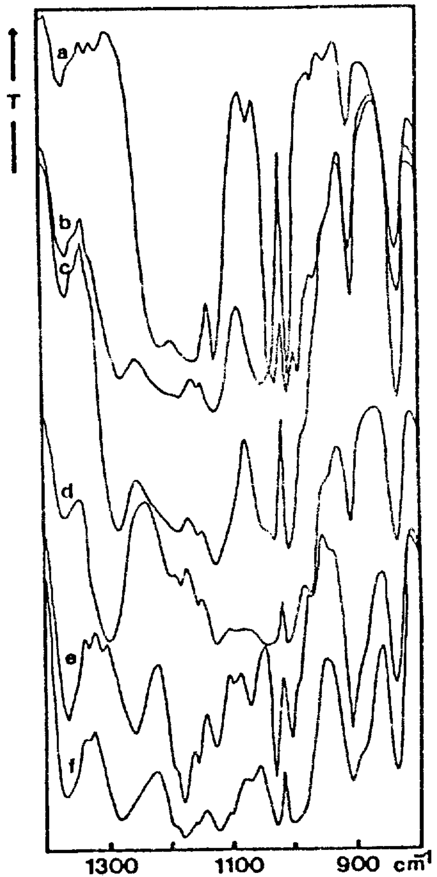


Figure 3. Infrared spectra of dehydrated transition metal ionomers in the 1400-800 cm^{-1} region, (a) hydrated 15.8% PSSA-Ni(II), (b) 15.8% PSSA-Ni(II), (c) 12.8% PSSA-Co(II), (d) 12.8% PSSA-Cr(III), (e) 12.8% PSSA-Rh(III), (f) 12.8% PSSA-Ru(III). All of the ionomer films except (a) are dehydrated.

In these hydrated transition metal ionomers, changing the ionic site concentration from 12.8% to 15.8%, to 20.1% does not change the IR spectra significantly, except for increasing the intensities of the SO_3^- related bands, as the ionic site concentration increases.

The spectra of the 6.9% ionomers show that no ion-exchange is achieved by Method A. The 6.9% PSSA-H inomer is known to form ionic domains which are accessible to metal cations over longer times. When the ionomers were made by Method B, the ion-exchange was complete, as shown by their IR spectra. The difference in effectiveness of the two methods of ion exchange is primarily a result of the low rate of solvated cation transport in films with low sulfonate concentration, since these films are largely polystyrene-like.

C. IR spectra of dehydrated transition metal ionomers. Dehydration of the hydrated transition metal ionomers is expected to cause structural changes since direct interaction is expected between the sulfonate groups and the dehydrated transition metal cations. One consequence of direct interaction may be cross-linking of the anion-contai-

Table 3. Typical Infrared Spectral Data of Dehydrated Transition Metal PSSA Ionomers (cm^{-1})

Ionomers	$^{a}\nu a(SO_3^-)$	$\nu s(SO_3^-)$	$\delta(SOM)$
^{b}PSSA-Fe(III)	1273, 1143	1036	a
PSSA-Co(II)	1282, 1128	1059 (sh)	985 (sh)
PSSA-Ni(II)	1279, 1130	1054	993
PSSA-Cr(III)	1295, 1128	1040	975
PSSA-Ru(III)	1283, 1124	1031	990 (sh)
PSSA-Rh(III)	1275, 1125	1040 (sh)	985 (sh)

^{a}Splitted due to the removal of degeneracy. ^{b}Data from Zundel's results. a Not reported.

ning chains by polyvalent cations, but other forms of ion aggregation are possible as well.

Structural changes of this sort should affect the glass transition temperatures(Tg) and related physical properties of the transition metal ionomers. These changes may affect the vibrational spectra, since the degeneracy that the antisymmetric stretching vibration has when the SO_3^- groups have C_{3v} local symmetry may be removed. Such reduction of the C_{3v} local symmetry would result in a splitting of the Va(SO_3^-) band at about 1210 cm^{-1} into two bands.[19] Thus, the position of the symmetric stretching vibration of the $-SO_3^-$ groups at about 1040 cm^{-1} should not be appreciably influenced by the metal cations. The magnitude of the splitting of the $\nu a(SO_3^-)$ band near 1200 cm^{-1} should increase with the strength of the interaction of the cations with the anion if the interaction is primarily ionic.

In the IR spectra of dehydrated transition metal ionomers, four new bands are observed in the 1300-900 cm^{-1} region (see Figure 3 and Table 3). The two bands at about 1280 and 1128 cm^{-1} are ascribed to a $\nu a(SO_3^-)$, corresponding to the splitting of the degenerate band in the dehydrated forms. The band at about 1128 cm^{-1} could be the same band of the in-plane skeletal vibration of the benzene ring, shown in the hydrated transition metal ionomers. However, these bands become clearly broadened after dehydration and they are different in shape from those shown in hydrated transition metal ionomers. Therefore, since these two bands due to $\nu a(SO_3^-)$ and the in-plane skeletal vibration of the benzene ring with the $-SO_3^-$ substituents are expected to appear in dehydrated transition metal ionomers, the two bands are believed to be superimposed at about 1128 cm^{-1}. The splittings of the degenerated band were found not to be affected greatly by metal cations or by their oxidation states. This means that the roles of the SO_3 groups as ligands are similar in each case, and that they coordinate rather than simply interact ionically with the cations.

The band at 1040 cm^{-1} is assigned to $\nu s(SO_3^-)$ and the band at 980 cm^{-1} is tentatively assigned to S-O-M stretching vibration with S-O single bond character, since these bands at about 980 cm^{-1} region were not observed in alkali or alkaline earth metal ionomers, but in various transition metal complexes containing sulfito (SO_3), or sulfinato(RSO_2) ligands.[21,22,23]

Far infrared spectra of transition metal PSSA ionomers. In the Far-IR spectra of PSSA[13], PSMA[24], PEMA[25], PFSA[26] ionomers, containing alkali or alkaline earth metal cations, strong broad bands are observed in 220-95 cm^{-1} region for alkali metal ions and in the 271-145 cm^{-1} region for alkaline earth metal ions. They are found to shift to lower frequency as the mass of the cations increases, and to higher frequency as the charge of cations is increased. The force field elements obtained from these sprctra have been interpreted in terms of coulombic interactions that are primarily ionic in nature.

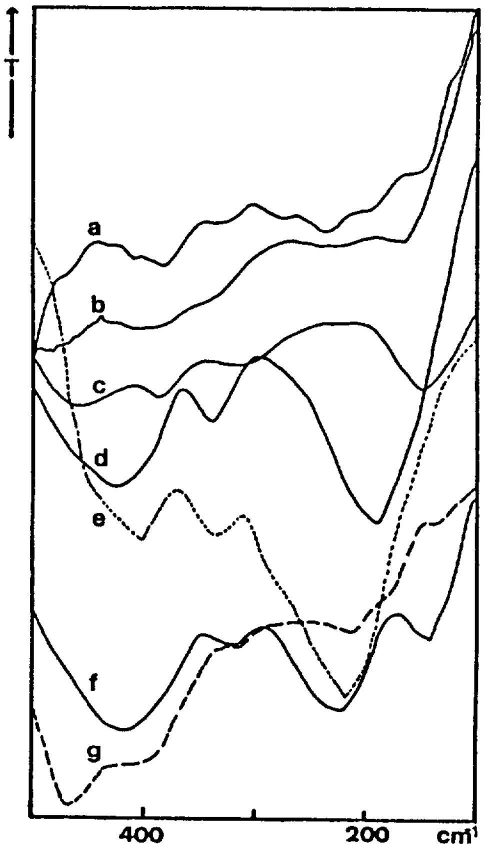


Figure 4. Far-IR spectra; (a) 15.8% PSSA-H, (b) hydrated 15.8% PSSA-Co(II), (c) 16.8% PSSA-Ba(II), (d) 15.8% PSSA-Co(II), (e) 15.8% PSSA-Ni(II), (f) 15.8% PSSA-Rh(III), (g) 15.8% PSSA-Ru (III). All film samples except (b) are dehydrated.

As shown in Figure 4, in the Far-IR spectra of dehydrated PSSA-H and hydrated transition metal PSSA ionomers in which there are not direct interactions between ionic groups, there are not strong features due to the polystyrene backbone or ionic groups.

But, when the transition metal ionomers are dehydrated, several strong broad bands are observed and they are quite different from the characteristic cation motion bands that were observed in alkali or alkaline earth metal ionomers.[13] These features are believed due to the metal-oxygen stretching, deformation of coordinated sulfonate ligands, and oxygen-metal-oxygen bending modes of sulfonate-coordinated transition metal ions, resulting from the coordination of sulfonate groups to metal cations. Those characteristic bands are typically found in the 500-40 cm^{-1} region and do not shift systemically with cation mass. The value of 475 cm^{-1} for the PSSA-Cr(III), ν(M-O) band may be compared to those found at 478 cm^{-1} for the chromium-oxygen stretch in polymeric Cr(III) ethoxide[27], at 463 cm^{-1} for $Cr(acac)_3$[28], and in the 400-540 cm^{-1} range for series of SO_3^{-2} transition metal complexes.[29]

There is little doubt of this assignment, but unfortunately

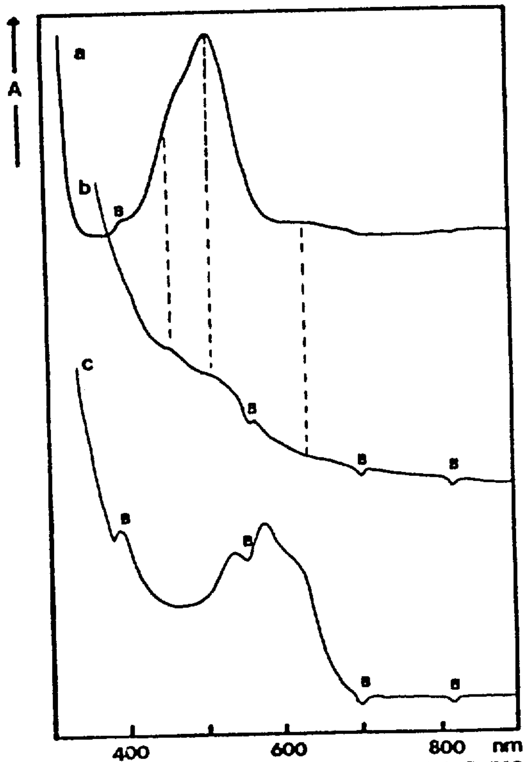


Figure 5. Visible spectra of (a) 0.1 M aqueous pink Co(NO$_3$)$_2$ solution, (b) hydrated 15.8% PSSA-Co(II) film (pale pink), (c) dehydrated 15.8% PSSA-Co(II) film(blue).

the most direct comparison, which would be with rigorously dehydrated Cr(III)-exchanged electrolytic PSSA materials, does not appear to be available in literature. Accordingly the bands in the 335-405 cm^{-1} region can be assigned to metal-oxygen stretching vibration and those in the 190-225 cm^{-1} are believed to correspond to coupled oxygen-metal-oxygen bending motion and/or MO$_3$S deformation.

It is interesting to note that there is no appreciable difference in Far-IR spectra resulting from the changes in ionic site concentrations of ionomers, in comparison to those of alkali or alkaline earth metal PSSA ionomers in which the cation motion bands shift to low frequency as the ionic site concentration increases.

Visible spectral study. The transition PSSA ionomers, containing Co(II), Ni(II), Cr(III), Ru(III), and Rh(III), become slightly colored after ion-exchange and the colors of those ionomer films change strikingly upon dehydration, as below:

metal ion	hydrated PSSA-M	dehydrated PSSA-M
Co(II)	pale pink	blue
Ni(II)	pale green	yellow
Cr(III)	pale violet	green
Ru(III)	dark brown	brownish black
Rh(III)	yellow	dark brown

These color changes are reversible upon hydration or dehydration and the intensities of the colors increase as the ionic site concentration increases.

In the case of both hydrated and dehydrated Ru(III) and Rh(III) PSSA ionomers, the UV/Vis spectra in the 190-900 nm region are dominated by strong charge transfer bands and this is expected for the ions in octahedral fields of weak ligands. But they leave no band in visible region by which a structural assignment can be made. Therefore, these ionomers are not treated further here, other than to note that the species are complexed by the SO$_3$ groups upon dehydration and have UV/Vis spectra that are consistent with approximate Oh coordination with the weak field SO$_3^-$ ligands, compared to already known Ru(III) or Rh(III)-related complexes.[30,31]

A. Vis spectra of PSSA-Co(II) ionomer. Of the cobalt ions, hydrated Co(II) salts or complexes that contain no other chromophores usually are red or pink and contain the [Co(H$_2$O)$_6$]$^{2+}$ ion or closely related octahedrally coordinated Co(II) ions.[30,31] The Vis spectrum of aqueous Co(NO$_3$)$_2$ solution of 0.06 M shows three absorption bands at 630(w), 510(s), an 460(sh) nm in the 380-900 nm region as shown in Figure 5. These are characteristic bands of [Co(H$_2$O)$_6$]$^{2+}$ ion, and can be assigned using simplified energy level diagram for d^7 Oh complex.[32,33]

The spectrum of hydrated PSSA-Co(II) film shows essentially the same absorption bands as above but with relatively weaker intensities. This suggests that the hydrated PSSA-Co ionomer contains the [Co(H$_2$O)$_6$]$^{2+}$ ions and that there is no significant interaction between the ionic groups, as concluded in the IR spectral study.

When the PSSA-Co(II) films are dehydrated, there are strong absorption bands at 610, 576, and 537 nm as shown in Figure 5. The color change from pink to blue in the Co(II) complexes has been observed frequently and is known to arise from the structural conversion from octahedral(pink) to tetrahedral(blue).[30]

Considering the energy level diagram for d^7 tetrahedral cobalt[32], three electronic transitions are expected from the ground state ${}^4A_2$ to ${}^4T_2$, ${}^4T_1$ and ${}^4T_1(P)$.[33] In typical electronic spectra of Td cobalt complexes, the first transition to ${}^4T_2$ is observed in the IR region(3,000-5,000 cm^{-1}) and the band, corresponding to second transition to ${}^4T_1$ is usually broad and appears in the near IR region. The band due to third transition to ${}^4T_1(P)$ is intense, broad and usually exhibits very complicated features, resulting from the spin-orbital coupling effects.[33]

The blue color which is frequently characteristic of the tetrahedral cobalt arises from this third transition, appearing in the 500-660nm region. Accordingly, the intense bands at 610, 576, and 537 nm are assigned to the transition from ${}^4A_2$ to ${}^4T_1(P)$ and the conclusion is drawn that the dehydrated PSSA-Co(II) ionomers contain tetrahedral cobalt ions. This is thought to be reasonable in part since each cobaltous ion is expected to interact two sulfonate groups because of the charge balance between them.

The possibility that the Co(II) species is square planar in the ionomer is ruled out by those spectra since such square complexes exhibit a broad band near 500 nm, while the tetrahedral complexes show intense multiple absorption in 540-720 nm region.[31]

B. Vis spectra of PSSA-Ni(II) ionomers. In the visible spectrum of aqueous Ni(NO$_3$)$_2$ solution(0.1 M), there bands at 728, 655, and 392 nm are observed in the 900-300 nm region. According to the energy level diagram for d^8 octahedral ions[30], thet can be easily assigned.

The visible spectrum of hydrated PSSA-Ni(II) ionomer films exhibits essentially the same bands as those of Ni(H$_2$O)$_6{}^{2+}$ though their intensities are much weaker. Therefore, as in the hydrated PSSA-Co(II), the hydrated PSSA-Ni

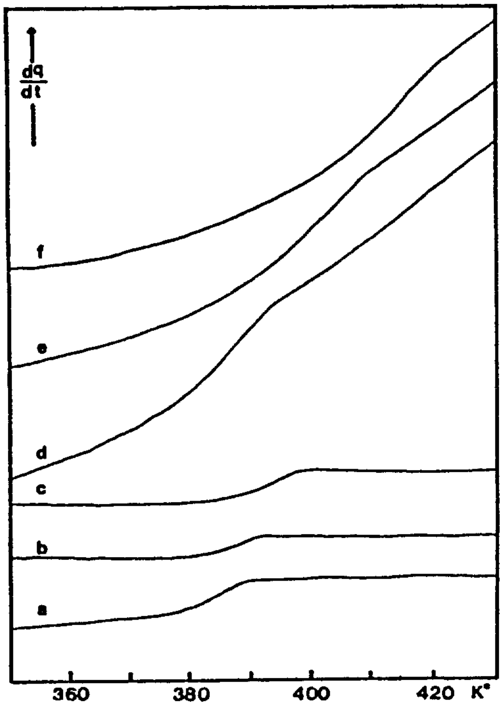


Figure 6. Thermograms of PSSA-H ionomer films: (a) h. 6.9%, (b) h. 12.8%, (c) h. 15.8%, (d) d. 6.9%, (f) d. 12.8%, (g) d. 15.8%, where h; hydrated, d; dehydrated.

(II) ionomer is also believed to contain the $Ni(H_2O)_6{}^{2+}$ species without direct interactions between the sulfonate groups and the Ni(II) ions.

In the case of dehydrated PSSA-Ni(II) ionomer, the color changed from pale green to yellow after dehydration and, in its visible spectrum, there are two absorption bands at 450 and 325 nm, which are quite similar to those of the square planar $[Ni(CN)_4]^{2-}$ complex(444 and 328 nm).

For the vast majority of four coordinated Ni(II) complexes with d^8 configuration, the square planar geometry is preferred since the planar ligand set causes one of the d orbitals to be uniquely high in energy and the eight electrons can occupy the other four d orbitals but leave this strongly antibonding one vacant. The square planar Ni(II) complexes are typically red or yellow although purple and green examples are known. The majority of these complexes exhibit a strong band in the 660-400 nm region and in many cases a second more intense band between 434-300 nm region. Usually the first band is assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition, and the second band to the ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition.[31,33] Thus, the two bands at 450 and 325 nm are believed to arise from the square planar Ni(II) and are assigned in the same manner as above.

Other possible structural types for Ni(II) in the dehydrated PSSA ionomer could be tetrahedral, trigonal-bipyramidal, or square-pyramidal, but these possibilities are ruled out since their visible spectra are quite dissimilar from that of dehydrated PSSA-Ni(II) ionomer film[31]

C. Visible spectra of PSSA-Cr(III) ionomer. A large number of Cr(III) complexes are hexacoordinated with a few exceptions and these six-coordinate chromium(III) compounds are generally green or violet in color.[30,31]

In the visible spectrum of the violet aqueous solution of $Cr(NO_3)_3$, four absorption bands at 670(sh), 574, 408, and 282 nm are observed. These are readily assigned to the transitions from ${}^4A_{2g}$ to ${}^2T_{1g}({}^2E_g)$, ${}^4T_{2g}$, ${}^4T_{1g}(F)$, and ${}^4T_{1g}(P)$ according to the Tanabe-Sugano diagram for hexaaquo chromium (III) ion.

Table 4. Tg Data of PSSA Ionomers

Ionomers PSSA-H	Tg(h)[a] °C	Tg(d)[b] °C	Ionomers PSSA-Cr(III)	Tg(h)[a] °C	Tg(d)[b] °C
6.9%	106	106			
12.8%	110	116	12.8%	115	–
15.8%	114	132	15.8%	128	–
PSSA-Co(II)			PSSA-Ru(III)[a]		
6.9%	111	117			
12.8%	114	–	12.8%	105	–
15.8%	132	–	15.8%	144	–
PSSA-Ni(II)			PSSA-Rh(III)[a]		
6.9%	115	123			
12.8%	106	–	12.8%	112	–
15.8%	115	–	15.8%	115	–

[a] h: hydrated. [b] d: dehydrated at 110 °C in vacuum for 2 days. a: approximately 70-80% ion-exchanged.

The spectrum of hydrated PSSA-Cr(III) ionomer film shows that the $[Cr(H_2O)_6]^{3+}$ species is present even though the intensities of the bands are weak. When the same film was dehydrated, its color changed from pale violet to green and its spectrum shows relatively strong bands at 450, 642, 665, and 685(sh) nm, which are quite similar to those of a large number of six-coordinated Cr(III) complexes in basically octahedral structure.[31] At this stage, it is difficult to make specific assignments, but the Cr(III) ion is predicted to interact with three sulfonate groups on the basis of charge balance between them, and their structure is expected to be distorted from the regular octahedral in that the sulfonate ligand could coordinate as a unidentate, bidentate, or tridentate, resulting in distorted octahedral structures of C_3, C_{3v}, C_{4v}, or D_{4h} symmetry.

Thus, while specific assignments can be made by simply assuming near Oh geometry and the Cr(III) in dehydrated PSSA ionomer is believed to have basically this structure, all that can be taken from the visible spectral data is that dehydration does cause the structure to change. This is important, though, because when combined with the IR data it shows that the sulfonates become the primary coordinating ligands and cross-link the PSSA inonmers through coordinative covalent bonds. Morever, it shows that the dehydration affects the coordination geometry.

Thermal analysis of PSSA ionomers. Incorporation of ionic species into hydrocarbon polymers is well known to exert a profound effect on the glass transition temperature (Tg).[34,35,36] Accordingly, the presence of transition metal ions in PSSA ionomer also may be expected to affect Tg significantly, since the anionic sulfonate groups could be cross-linked through their coordination to transition metal cations.

Such coordinative cross-linking should vary with cation, hydration, and other factors. Also, it should be mentioned that, when the density of cross-links is high, the glass transition region is broadened, and the Tg may not be observable at all in highly cross-linked materials.[36]

A Glass transition temperatures of PSSA-H ionomers. As shown in Figure 6 and Table 5, the Tg values of hydrated PSSA-H ionomers are found to increase as the ex-

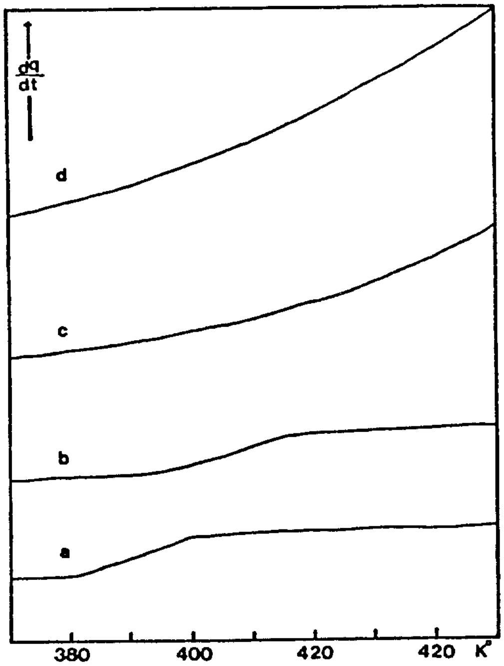
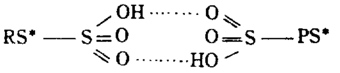


Figure 7. Thermograms of PSSA ionomer containing Co(II): (a) h. 12.8%, (b) h. 15.8%, (c) d. 12.8%, (d) d. 15.8%, where h; hydrated, d; dehydrated.

tent of sulfonication increased. When the PSSA-H ionomers are dehydrated, the glass transition range becomes very broad. This indicates the effective cross-linking is greater than it is in hydrated PSSA-H ionomers. As concluded in the IR spectral study section, When the PSSA-H ionomers are hydrated, there are many water molecules in the hydrophilic ionic domains. This extensive hydrolysis prevents strong hydrogen bonding between the $-SO_3^-$ groups, and they retain their C_{3v} local symmetry. But when those water molecules are removed by dehydration, the acid groups can form stronger hydrogen-bonded dimers or even more highly ordered structure. The dimer is shown below:



$$RS^* - S(=O)(=O)(OH) \cdots\cdots (HO)(O=)(O=)S - PS^*$$

PS*; polystyrene backbone

When the sulfonate groups are cross-linked to one another by relatively strong hydrogen bonds, the segmental mobility of the polymer is appreciably lowered and the Tg is increased. This apparently occurs in the case of 12.8% and 15.8% PSSA-H ionomers. The Tg values of the 6.9% PSSA-H ionomers is the same whether they are hydrated or dehydrated, even though the transition range becomes broadened after dehydration. This can be interpreted by noting that at low ionic site concentration the spacing between the sulfonated groups increases, and consequently the interaction between the ionic groups does not perturb the segmental mobility of polymer backbone significantly.

B. Glass transition temperatures of transition metal PSSA ionomers. The hydrated transition metal PSSA ionomers exhibit typical glass transitions as shown in Figure 7. For the 6.9% transition metal PSSA ionomers prepared by Method B, which were found to be completely ion-exchanged, Tg was observed at 111 °C and at 115 °C for PSSA-Co(II) and PSSA-Ni(II), respectively. In comparison with the values of PSSA-H ionomers, these are increased by 5 °C and 9 °C, respectively. This suggests that there is some relatively stronger association of the ionic groups upon the incorporation of metal cations, resulting in the increases of the Tg. However, the cations were found to be highly solvated by water molecules as discussed in previous sections. Thus, the association is not that of direct coordination. Presumably the presence of the cations simply strains the polymer backbone by increasing the volume around which they must arrange.

As to the hydrated 12.8% PSSA-Co(II), -Cr(III), and -Rh (III) ionomers, the Tg values are higher by 2-5 °C than that of the hydrated 12.8% PSSA-H ionomer. But in the case of PSSA-Ni(II) and -Ru(III), the glass transition temperatures were observed at 106 °C and 105 °C. Since all of these ionomers have a relatively higher water content and the Tg values have an uncertainty of at least ±2 °C, it appears that the fluctuations of Tg are largely volume effects as aforementioned.

The Tg values of hydrated 15.8% transition metal PSSA ionomers were found to increase up to 30 °C, but in PSSA-Ni(II) and -Rh(III), the Tg values are quite close to that of hydrated 15.8% PSSA-H ionomer despite the presence of transition metal cations.

The clear result of these measurements is that while the Tg of hydrated transition metal PSSA ionomers increases somewhat as the ionic site concentration increases, they are profoundly affected by the degree of hydration, since the ionic species are strongly but differently solvated by water molecules.

Thus, the measured Tg values of hydrated transition metal ionomers do not depend directly on the nature of metal cations or on their oxidation states, but very indirectly on the way that the solvation of the cations and the ionomers occur. In the case of the dehydrated 12.8% and 15.8% transition metal PSSA ionomers, no glass transition was observed in the 25-220 °C region, as predicted. On the basis of IR and Visible spectral study, this result is believed due to the direct coordination of the sulfonate groups to the transition metal cations, which leads to the formation of highly cross-linked structure.

In 6.9% PSSA ionomers, the glass transition is always observed even after they are completely ion-exchanged whether they are hydrated or dehydrated. This indicates that, at this ionic site concentration, the glass transition is due principally to the segmental mobility of polymer backbone which can occur even when strong cross-links are present because of the relatively larger spacings between adjacent sulfonated styrene groups. In other words, in this case, the density of cross-linking is relatively low though its strength is quite strong. Relative to PSSA-H ionomer, hydration of the ionomer decreases the Tg and the presence of the transition metal ions increases it to a small extent.

Acknowledgments. We gratefully acknowledge the partial support of this work by the ONR of U.S.A. and I.W. Shim is very grateful to the Korea Science and Engineering Foundation for financial support. The authors are thankful to Dr. R.D. Lundberg of Exxon(U.S.A.) for kindly providing the PSSA materials.

References

1. Holliday, I., Ed., "Ionic Polymers", Applied Science, London, 1975.

2. Eisenberg, A., Ed., "Ions in Polymers", *Am. Chem. Soc.*, Washington, D.C., 1980.
3. D. G. Pieff, R. A. Weiss and R. D. Lundberg, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1503 (1982).
4. T. D. Gierke, G .E. Munn and F. C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1687 (1981).
5. R. A. Weiss, J. Lefelor, and H. Toriumi, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 661 (1983).
6. Ogumi, Z., Takehara, Z., and Yoshizawa, S., *J. Electrochem. Soc.-Electrochem. Sci., and Technol.*, **131**, 769 (1984).
7. N. E. Prieto and C. R. Martin, *J. Electrochem. Soc.-Electrochem. Sci. and Technol.*, **131**, 751 (1984).
8. D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **106**, 59 (1984).
9. F. J. Waller, *U. S. Patent* 4,414,409 (1983).
10. W. H.Kao and T. Kuwana, *J. Am. Chem. Soc.*, **106**, 473 (1984).
11. W. Siebourg, R. D. Lndberg, and R. W. Lenz, *Macromolecules*, **13**, 1013 (1980).
12. R. D. Lundberg and R. R. Philips, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1143 (1982).
13. V. D. Mattera, Jr. and W. M. Risen, Jr., *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 67 (1984).
14. W. M. Risen, Jr., *et al.*, *Amer. Chem. Soc. Symposium Series* **302**, (1986), and references there in.
15. I. W. Shim, V. D. Mattera, Jr., and W.M. Risen, Jr., *J. Catal.*, **94**, 531 (1985).
16. V. D. Mattera, Jr., P. J. Squattrito, and W. M. Risen, Jr., *Inorg. Chem.*, **23**, 3597 (1984).
17. H. S. Makowski, R. D. Lundberg, and G. H. Snigbal, *U. S. Patent*, 3,870,841 (1975).
18. C. Y. Liang and S. Krimm, *J. Polym. Sci.*, **27**, 241 (1958).
19. G. Zundel, "Hydration and Intermolecular Interaction", Academic, New York, 1969.
20. G. Kresze, E. Ropte, and B. Schrader, *Spectrochim. Acta.*, **21**, 1633 (1965).
21. E. Linder and G. Vitzthum, *Chem. Ber.* **102**, 4026 (1969).
22. B. Nyberg and R. Larsson, *Acta Chem. Scandina*, **27**, 63 (1973).
23. G. Newman and D.B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).
24. G. B. Rouse, A. J. Tsatsas, A. Eisenberg, and W.M. Risen, Jr., *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 81 (1979).
25. A. T. Tsatsas and W. M. Risen, Jr., *Chem. Phy. Lett.*, **7**, 354 (1970).
26. S. L. Peluso, A. T. Tsatsas, and W. M. Risen, Jr., *ONR Technical Report* 79-01(U.S.A.).
27. D. A. Brown, D. Cunningham, and W. K. Glass, *J. Chem. Soc.*(A), 1504 (1968).
28. K. Nakamoto, C. Udovich, and J. Takemoto, *J. Am. Chem. Soc.*, **92**, 3973 (1970).
29. Y. Kanamura and K. Nakamoto, *Inorg. Chem.*, **14**, 63 (1975).
30. "Electronic Structure and Magnetism of Inorganic Compounds: Specialist Periodical Reports", Vol. 1-5, The Chemical Society, Burlington House, London
31. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier Publishing Company, 1984.
32. B. N. Figgis, "Introduction to Ligand Fields", Interscience Publishers, 1966.
33. D. Sutton, "Electronic Spectra of Transition Metal Complexes", Mcgraw-Hill, London, 1968.
34. R. J. Young, "Introduction to Polymers" Chapmann and Hall, New York, 1981.
35. P. J. Flory, "Principles of Polymer Chemistry", Cornell Univ. Press, London, 1953.
36. A. Eisenberg and M. King, "Ion Containing Polymers; Physical Properties and Structures", Academic, New York, 1977.
37. J. H. Gibbs, "In Modern aspects of the Vitreous state", J. D. Markenzie, Ed., Buttersworth, Washington, D.C. 1960.
38. R. A. Weiss, *J. Polym. Sci. Polm. Phys. Ed.*, **20**, 65 (1982).

Cross Interaction Constants As a Measure of the Transition State Structure (Part VI). Nucleophilic Substitution Reactions of Benzyl Chlorides with Anilines and Benzylamines

Ikchoon Lee*, Chul Huh, Han Joong Koh, and Hai Whang Lee

Department of Chemistry, Inha University, Inchon 402-751. Received July 28, 1988

Results of kinetic studies on the reactions of benzyl chlorides with anilines and benzylamines are reported. Analyses of the cross interaction constants relevant to the degree of bond formation, ρ_{XY} and λ_{XY}, are carried out. The magnitudes of the two parameters indicated that the degree of bond formation in the transition state is the typical of that expected for an S_N2 reaction, but the reactions with benzylamines appear to have a slightly less degree of bond formation compared with the reactions with anilines.

Introduction

The nucleophilic substitution (S_N) reaction of benzyl chlorides has been a subject of numerous studies[1] because of its mechanistic versatility[2]. Some of the reactions including solvolyses exhibited borderline behaviors[3] in the S_N1-S_N2