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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TR-83-04	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A Far Infrared Study of Ionic Interactions in Polystyrene Sulfonic Acid Ionomers		5. TYPE OF REPORT & PERIOD COVERED Technical
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Vincent D. Mattera, Jr. and William M. Risen, Jr.		8. CONTRACT OR GRANT NUMBER(s) NO0014-75-C-0883 NR-051-539
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Brown University Providence, Rhode Island 02912		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ONR-NO0014-75-C-0883 NR-051-539
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research United States Navy		12. REPORT DATE March 10, 1983
		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution Unlimited; Approved for Public Release		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Ionomer, Ion motion, ionic domains, polystyrene, polystyrene sulfonic acid, sulfonated polystyrene		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The far-infrared spectra of polystyrene sulfonic acid (PSSA) ionomer films containing alkali and alkaline earth ions have been studied, and strong, broad bands whose frequencies are cation-dependent, have been observed and assigned to cation-motion. The force field elements for cations vibrating at sulfonate-containing sites have been obtained for different models of the cation-motion vibration. The effects of hydration, dehydration and thermal annealing are discussed in light of ion-clustering in these materials.		

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A Far Infrared Study of Ionic Interactions in Polystyrene Sulfonic Acid Ionomers

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Introduction

Studies of ion-containing organic polymers (ionomers) indicate that some of their materials-properties depend on the extent of ion aggregation (1-3). In general, ion aggregation is expected to occur in ionomers since the ions are present in the medium of low dielectric constant of the polymer network. As the concentration of neutralized (e.g. alkali cation-containing) acid groups increases, the probability of domain formation (formation of ionic clusters) increases as well. Above a critical concentration ionic domain formation can lead to microphase separation resulting in a dispersed ionic phase too small to scatter visible light but large enough to affect the mechanical and rheological properties of the materials. The concentration at which clustering is observable experimentally often is found to be below 10 mole percent (ion composition).

The solution properties of a new class of ionomers derived from polystyrene sulfonic acid (PSSA) have been studied extensively (4-6), but the solid analogs are less well characterized. Of particular interest, there have been no direct studies of the ionic interactions that are largely responsible for their glass transition, viscoelastic, ion diffusion and related properties. However, several studies of ion-clustering in solid state PSSA ionomers have been reported recently. On the basis of the effect of varying metal sulfonate composition on the viscoelastic properties of PSSA ionomers, Rigdahl and Eisenberg concluded that the onset of ion-clustering occurs at about 6 mole percent (7). This is supported by the fluorescence studies of Okamoto, et al. (8), which indicated that no appreciable ion-aggregation occurs below 6 mole percent. However, Cooper and co-workers reported that the results of their (EXAFS) experiments indicate that ion clustering is present at about 3 mole percent and that short range ordering exists within the clusters (9). Lundberg and co-workers, who developed this class of ionomers, reported that their SAXS experiments indicate that clusters

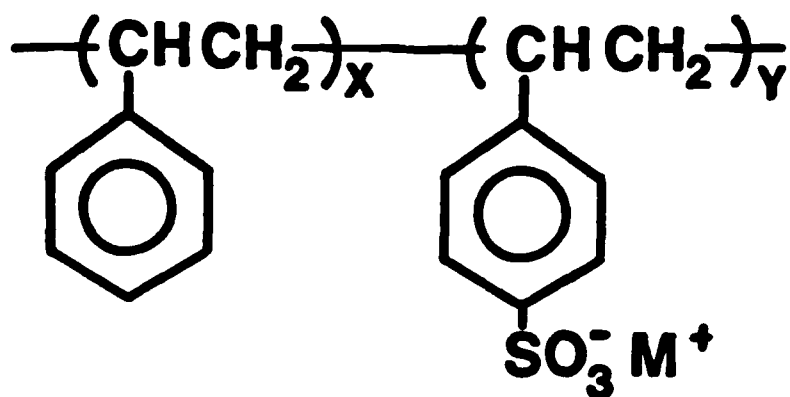
are present at compositions as low as 3 mole percent (10), resulting in a microphase separated material. In addition, a small angle neutron scattering (SANS) study of PSSA ionomers suggests the presence of ionic clusters (11). The general picture that develops from these studies is that ion clusters tend to form in PSSA ionomers, certainly below 10 mole percent.

We have reported studies of the cation-site interactions in other ionomers; polyethylene methacrylic acid (PEMA) (12,13), polystyrene methacrylic acid (PSMA) (14), and Nafion-type, perfluorocarbon sulfonic acid (PFSA) (15). The observed low frequency infrared vibrations were assigned to the motion of the cations in the potential field of their counterions. In these studies it was shown how the magnitude of the cation-anion site interactions depend on the degree of clustering, the extent of hydration and the nature of the cation and anionic polymer.

The relationship between PSSA ionomer properties and systematic molecular changes such as the variation of the cation, M^{+n} , and the sulfonate concentration were investigated in order to provide an understanding of the ionic interactions. The forces acting between a cation and sulfonate site were probed by studying the vibrations in which the cation participates. The ionic interactions were found to be sensitive to the degree of hydration. Effective force constants are calculated and discussed in terms of several models for the cation-motion vibration. In addition, the effects of thermal annealing on the far infrared spectra are presented.

Experimental

Polystyrene sulfonic acid samples were provided kindly by Dr. R.D. Lundberg of the Exxon Research and Engineering Co. The synthesis has been described fully by Dr. Lundberg and co-workers elsewhere (16). The chemical composition of the materials can be represented as:



where M is a metal cation and the value of $y/(x+y)$ represents the mole fraction of sulfonate groups. Transparent films (25–350 μm) were obtained by dissolving powdered samples of the H^+ form in solutions of toluene/methanol (at a 9:1 volume ratio) or tetrahydrofuran and allowing for solvent evaporation at room temperature.

The ionomers were prepared by a simple ion-exchange process in which PSSA films were stirred in metal acetate-containing solutions of aqueous methanol and ethanol. Prior to recording their far infrared spectra, the films were removed from solution, rinsed with distilled water and wiped dry. The films were mounted in a special stainless steel cell, with IR or Far IR transmitting windows, whose temperature and pressure could be varied. Using this cell, the spectra could be taken in situ of films subjected to various thermal, dehydration, and other treatments. For dehydration criteria see footnote 28.

The infrared spectra of the ionomer films in the 50–500 cm^{-1} region were recorded with Digilab 14 and Digilab 15B FT-IR spectrometers. Each trace represents the average of at least 400 scans at 4 cm^{-1} resolution.

The materials and their spectra are labelled by a number designating the concentration of sulfonate groups followed by letters (Na, K, Rb, Cs, etc.) in parentheses indicating the ionomer forms of the polymer. The sulfonate composition (mole percent) of the samples studied and the associated spacing of sulfonate groups along the polystyrene backbone are indicated by the code number. Thus, PSSA 3.4 has 3.4 mole percent sulfonate and the sulfonate groups are separated,

on the average, by 30 unsulfonated styrene groups. The analog's code, mole percent sulfonate and average spacing are: (6.9), 6.9%, 15 groups; (12.7), 12.7%, 8 groups; and, (16.7), 16.7%, 6 groups. The mid infrared spectra of all of the ionomer films were studied carefully to determine the extent of ion-exchange. For each sample reported here, exchange was found to be essentially 100% complete by comparing its mid infrared spectrum to that of a similarly sulfonated H-PSSA. The conditions under which the spectra were taken (sample treatment) are specified in the figures or the Results section.

Results

Cation-Motion Vibrations

The far infrared spectra of the alkali and alkaline earth PSSA ionomers were recorded in transmittance. As shown in Figure 1 for the PSSA (6.9) Na, K, Rb and Cs ionomers and in Figure 2 for the PSSA (6.9) Ca, Sr and Ba ionomer films, which were dehydrated in vacuo at ca. 170°C, the dominant feature in each case is a broad band below 300 cm^{-1} which shifts to lower frequency as the mass of the cation increases. Similar results are obtained with the ionomer films studied at other sulfonate compositions. Table 1 lists the cation-motion frequencies observed at different sulfonate compositions for dehydrated ionomer films. In general, the error associated with the estimate of ω_0 is the order of $\pm 5 \text{ cm}^{-1}$. The higher vibrational frequencies observed for the PSSA Li^+ (470 cm^{-1}) and Mg^{+2} (445 cm^{-1}) ionomers suggest that the cation-sulfonate forces are covalent in nature and, therefore, are not treated here.

Effect of Hydration

It has been suggested that the presence of water can influence the structural, mechanical and thermodynamic properties of ionomers (18). In order to determine how the cation-motion bands were affected by the presence of solvent in the films

as a result of the ion-exchange process, dehydration studies were performed. In all cases, the cation-motion bands are better defined after dehydration since infrared absorptions of water are particularly strong in this spectral region. Figure 3 shows the far infrared spectrum of PSSA (6.9) Ba before dehydration (W) and after dehydration at ca. 170°C (D). There is an apparent shift toward lower frequencies upon dehydration. Similar effects are observed in other ionomer films.

Effect of Annealing

The effect of annealing the films above their glass transition temperatures (19) was studied to determine whether the cation-motion bands could be influenced by short range configurational rearrangements such as ionic domain formation. For example, in Figure 4 is shown the spectrum of PSSA (16.7) Sr which was dehydrated at ca. 170°C in vacuo (D) and annealed at ca. 200°C for 24 hr. (A). It is clear that while the cation-motion frequency remains unchanged, the general shape of the band is better defined and narrower in the spectrum of the annealed film.

Discussion

The results clearly demonstrate that the "cation-motion" vibrational bands depend on the mass and charge of the cation, as well as hydration and thermal annealing. Two approaches can be taken in order to assign the nature of the vibration.

First, it is necessary to assign these bands. Using a pseudo-diatomic oscillator model and letting the reduced mass vary as that of the cation permits us to show that the vibrational frequency (ω_0) depends strongly on the cation mass, (m_{C+n}). As shown in Figure 5, plots of ω_0 vs $(m_{C+n})^{-1/2}$ are nearly linear for the PSSA (6.9) M ionomers. Similar plots are observed for ionomers of different sulfonate composition. These results suggest that the vibration is due primarily to the cation-anion site vibration. That is, it is due to the motion of the cation

under the influence of the Coulombic (electrostatic) field of the sulfonate group. The force constants one obtains from such a treatment, $F(C^{+n})$, are of the same order of magnitude for members of a given group while those for the Group IIA ions are greater than the Group IA ions. The interpretation is not complete, though, for two reasons. First, this vibrational model is clearly not useful for any purpose other than making initial band assignments and it requires the cation's surrounding to be infinitely heavy. Second, since the Coulombic attraction part of the field due to the cation decreases with increasing ionic radius, the effective force constants for the $Cs^+ - SO_3^-$ interaction should be less than that of $Na^+ - SO_3^-$.

To find the force field elements and their variation with cation more accurately, the reduced mass, μ , is found for vibrational models in which the cation is coordinated to several oxygens of the neighboring sulfonate groups. This is done to recognize the spatial coordination of the cations and the fact that a reasonable vibrational model requires motion of the oxygens, at least, to conserve linear momentum. While the exact geometry is not known, of course, the cation may be taken as being surrounded by four or six lighter atoms. Since several of these must be oxygens, we approximate the simplest vibrating entity as a cation surrounded tetrahedrally or octahedrally by oxygen atoms. The only infrared active stretching mode of a cation in an octahedral field, MO_6 , is the T_{1u} mode whose reduced mass is $\mu(T_{1u}) = (m_{C^+}m_O)/(2m_O + m_{C^+})$ where m_O is the mass of an oxygen atom and m_{C^+} is the mass of the cation. In the case of a tetrahedrally surrounded cation, the reduced mass for the infrared active T_2 stretching mode is employed. In Table 2 are listed the vibrational frequencies, the reduced masses and the effective cation-sulfonate force constants, $F(T_{1u})$ and $F(T_2)$, calculated for the PSSA (6.9) M ionomers using $\mu(T_{1u})$ and $\mu(T_2)$, respectively. The values of $F(T_{1u})$ and $F(T_2)$ are of the same order of magnitude as those of the metal-cation-anion site force fields evaluated from the spectra of PEMA (12,13), PSMA (14) and PFSA (Nafion) (15) ionomers. There are, however, significant differences in the magnitudes of the

force fields in PSSA systems. The results indicate that the ion-site force field of the Na^+ ionomer is greater than that of the Cs^+ ionomer. This suggests the importance of the Coulombic attractive part of the ion-multipole field of the cation in determining the force constants and, thus, the cation-motion frequencies.

It is interesting to note that in an exhaustive study of the effect of hydration on the ionic interactions of polyelectrolyte salts, Zundel (17) calculated the relative strength of the Coulombic field of the cation on the SO_3^- group in covalently crosslinked PSSA. Although the polymer network in that system differs from PSSA ionomers, important terms in the ionic force equations are similar. We turn our attention to the effects of these types of forces on chemical and physical properties, and their modification by additional treatment. Hydration results in high local charge-screening effects, equivalent to immersion in a high dielectric constant medium and, therefore, changes the morphology of ionic clusters from that of the anhydrous materials. The effect of hydration on the ionic forces will be exerted through both bonding (H-bonds), and ion-dipole interactions of H_2O with the cation and sulfonate group (17). Our results show that for PSSA ionomers the cation-motion frequency decreases and the band shape sharpens upon dehydration. This is interpreted as being due to an increased interaction between the sulfonate groups and the cation as solvent is removed. While that is not surprising, the result also requires that the ionic structure be altered by dehydration. Similar conclusions were reached by Mauritz (21) who studied the effects of hydration on the mid infrared spectra of PFSA ionomers. These results are of particular interest with regard to ion-transport in the materials.

The ionic forces also affect the glass transition temperature (T_g), an intensive property of amorphous ionomers. Eisenberg (22) has suggested a relationship between T_g , the charge of the cation (q_{c+}) and the distance between cation and anion (r), which assumes that the cation-anion interactions limit the segmental mobility and

account for the increase in T_g relative to the ion-free polymer. Qualitatively, this suggests a direct relationship between T_g and the magnitude of the cation-sulfonate force constant, and we presently are studying the glass transition behavior (19) of the PSSA ionomer films used in the study. On initial DSC scans, we have observed sub- T_g endotherms that we think result from relief of stresses imposed by film preparation and thermal history. These preliminary results are supported by a recent study of the effect of aging on the thermal behavior of PSSA ionomers (23). Thus, it was of interest to investigate the effect of annealing on the cation-motion vibrations.

In general, the vibrational bands were sharpened and better defined after the films were annealed above T_g , as shown, for example, in Figure 4 by the spectrum of PSSA (16.7) Sr after dehydration (D) and after thermal annealing (A). However, within experimental error there is no change in ω_0 . The results of hydrating (W), dehydrating (D) and annealing (A) on the spectrum of PSSA (16.7) Ba are compared in Figure 7. These results are interpreted in terms of decreased intermolecular interactions at elevated temperature. In general, this is expected on thermodynamic grounds (24) and is consistent with but not proof of, the formation of ionic multiplets from ionic clusters at higher temperatures (25,26).

It was of interest to compare the spectra of PSSA ionomers as a function of sulfonate composition in light of the observation of a cluster mode present in the far infrared spectra of PSMA ionomers (14). A comparison of the far infrared spectra of PSSA (3.4), (6.9) and (16.7) Ba ionomers is shown in Figure 8. Overall, the value of ω_0 falls somewhat as the mole-percent sulfonate increases from 3.4 to 16.7. The Ba^{+2} ion-motion band in particular, undergoes an apparent shift toward lower frequencies with increasing sulfonate compositions. This is consistent with more cations being in large ionic clusters at higher sulfonate compositions, because the vibrations of cations in such domains are

expected to have both a larger effective mass and lower effective force constant since increased screening lowers the cation-sulfonate site attraction. This effect is most pronounced in K^+ and Ba^{+2} ionomers while no similar trend is apparent in the others. This is interesting because the K^+ ion ($r_{K^+} = 1.33 \text{ \AA}$) and Ba^{+2} ion ($r_{Ba^{+2}} = 1.34 \text{ \AA}$) are essentially the same size which suggests that some cation size-sensitive configurations may favor clustering interactions to enough of an extent to influence the morphology marginally.

Finally, it is useful to note how these cation-motion band observations compare with those we have made on other ionomers. In all cases, including PSMA, PEMA, PFSA and the presently considered PSSA, there are strong far infrared bands whose frequencies depend strongly on both the cation mass and the nature of the local anionic site. In the case of PSMA ionomers the (far infrared) band structures also depend on the aggregation of the ionic units such that ion-motion bands are observed for ions in both clusters and smaller aggregates. The anionic site in PSMA ionomers is a carboxyl group and the cation-motion vibrations occur at higher frequencies. For example Table 4 lists the values of ω_{C^+} for PEMA, PFSA and PSSA ionomers for comparable values of ion-composition. Of particular interest is the comparison between the PFSA and PSSA since the two sulfonate ionomers contain different polymeric backbones and the cluster morphology of PFSA with its teflon-like backbone has been studied (27). It is widely accepted that ionic domains of approximately 40 \AA in diameter are present in PFSA ionomers. The observation that the cation-motion frequencies of PFSA ionomers are lower than those of PSSA can be accounted for qualitatively by considering electronic and structural variations between the two ionomers. In contrast to PSSA, the electron withdrawing effect of the teflon-like backbone in PFSA ionomers is expected to result in a lower charge density on the SO_3^- groups and,

therefore, a decrease in the attractive part of the Coulombic potential, resulting in a lower cation-motion vibrational frequency. The lower frequencies observed in PFSA ionomers could simply be due to PFSA having larger ionic domains than PSSA, since the increased screening of the cation-sulfonate interactions combined with increased vibrational reduced mass in larger domains would cause shifts toward lower frequencies. Although these are conceptually different explanations, the domain size and charge distribution in the polymer are closely related.

Conclusions

A knowledge of the Coulombic forces acting in ionomers and how these forces depend on the anion-site concentration as well as the nature of the cation is useful in developing theories of ion-clustering in ionomers. The fact that the interionic forces in PSSA ionomers, as measured by the cation-anion site force field elements, do not vary strongly with increasing sulfonate composition, combined with the fact that the ion-exchanges were carried out at very low temperature suggests that a clustered or at least somewhat organized morphology may be present in the unneutralized (H^+ form) PSSA films as prepared. The introduction of the cations clearly does introduce strong ionic forces, and some manifestations of this should appear even though the forces do not seem to vary much with domain size (or at least sulfonate composition). First, the force fields should vary with cation-site Coulombic potential, as they do. Second, an additional relaxation mechanism related to T_g should be introduced. While it may not cause T_g to vary linearly or simply with cation-anionic forces, it can be manifested in broadening of the T_g transition range and variation of T_g with sulfonate composition.

Acknowledgments

This work was supported in part by the Office of Naval Research. The partial support and use of facilities of the Materials Research Laboratory,

sponsored by the National Science Foundation is gratefully acknowledged.

Helpful discussions with Dr. R.D. Lundberg, Exxon Research and Engineering Co. and E.I. Kamitsos, Brown University, are appreciated.

TABLE 1

Observed Cation-Motion Bands in PSSA Ionomers

Cation ^b	PSSA (3.4)	PSSA (6.9)	PSSA (12.7)	PSSA (16.7)
Na ⁺	220 cm ⁻¹	210 cm ⁻¹	a	210 cm ⁻¹
K ⁺	170	162	170 cm ⁻¹	155
Rb ⁺	120	120	120	116
Cs ⁺	100	100	100	95
Ca ⁺²	a	270	270	a
Sr ⁺²	180	177	175	170
Ba ⁺²	170	160	148	145

a. Results not included due to incomplete ion-exchange

b. Li and Mg PSSA data also obtained, please see text.

TABLE 2

Cation Motion Frequencies and Force Field Elements for 6.9% PSSA Ionomers^a

Cation	ω_0 (cm ⁻¹)	$F(C^{+n})$ (10 ² N m ⁻¹)	$F(T_2)$ (10 ² N m ⁻¹)	$F(T_{1u})$ (10 ² N m ⁻¹)
Na ⁺	210	0.60	0.22	0.17
K ⁺	162	0.61	0.16	0.14
Rb ⁺	120	0.73	0.11	0.10
Cs ⁺	100	0.78	0.08	0.08
Ca ⁺²	270	1.72	0.45	0.38
Sr ⁺²	177	1.62	0.25	0.22
Ba ⁺²	160	2.07	0.24	0.20

a) Here $F(C^+)$, $F(T_2)$, and $F(T_{1u})$ are the net force field elements for the cases described in the text; $F(T_2)$ for the T_2 stretch of $T_d MO_4$, $F(T_{1u})$ for the T_{1u} stretch of $O_h MO_6$, and $F(C^+)$ for a pseudo-diatomic model in which μ is the cation mass.

TABLE 3

Calculated Values of $F(T_{1u})$ for Different Ion Compositions

$$F(T_{1u}) \quad (10^2 \text{N}\cdot\text{m}^{-1})$$

Cation	PSSA (3.4)	PSSA (6.9)	PSSA (12.7)	PSSA (16.7)
Na ⁺	0.19	0.17	a	0.17
K ⁺	0.15	0.14	0.14	0.13
Rb ⁺	0.10	0.10	0.10	0.09
Cs ⁺	0.08	0.08	0.08	0.07
Ca ⁺²	a	0.38	0.38	a
Sr ⁺²	0.22	0.22	0.21	0.20
Ba ⁺²	0.22	0.20	0.17	0.16

a. Results not included due to incomplete ion-exchange

TABLE 4

A Comparison of Selected Vibrational Frequencies (ω_0 , cm^{-1}) for Three Different Ionomers

C^+	PEMA ^a	PSSA ^b	PFSA ^c
Na^+	230	210	180
K^+	180	162	150
Rb^+	d	120	110
Cs^+	135	100	90

a. Reference 13

b. This work, 6.9 mole % composition

c. Reference 15

d. Not reported

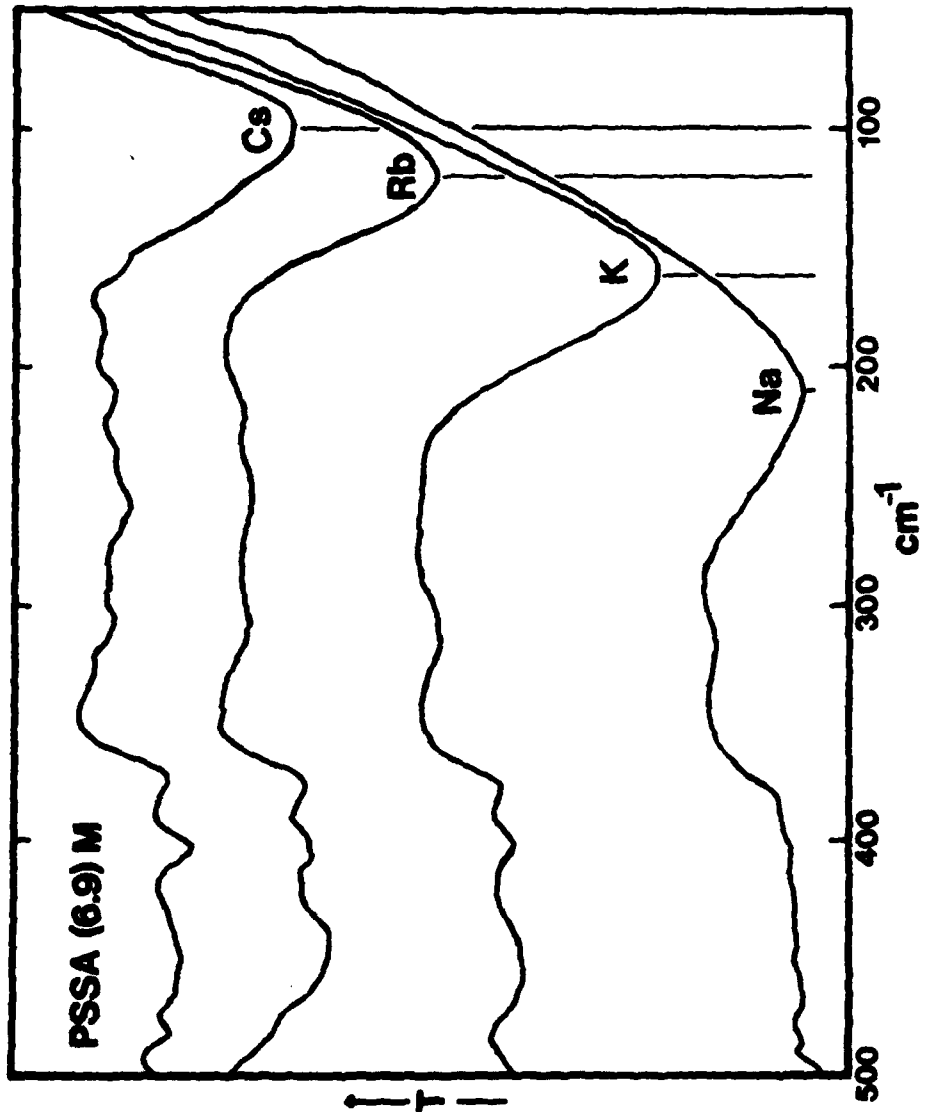
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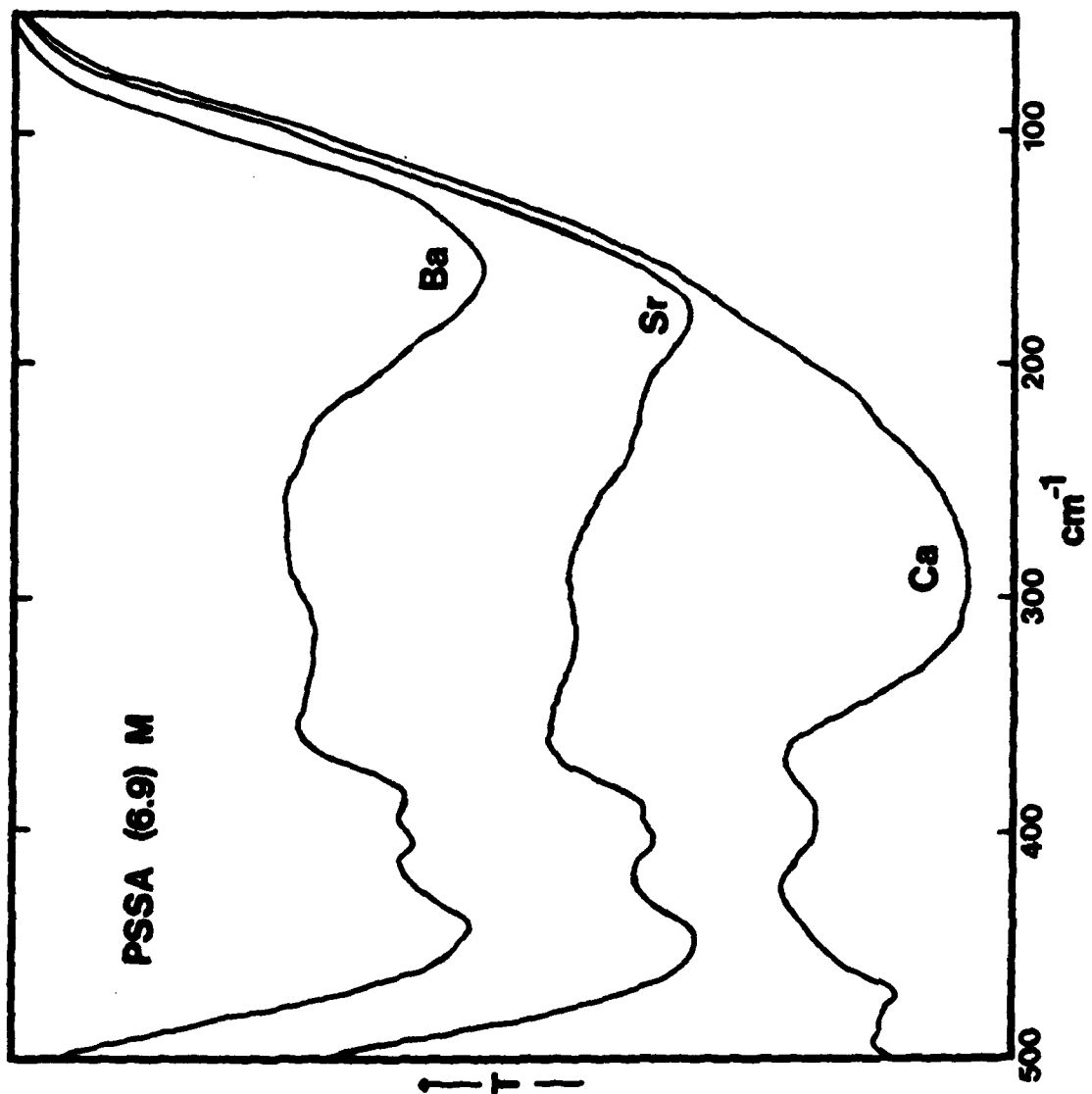
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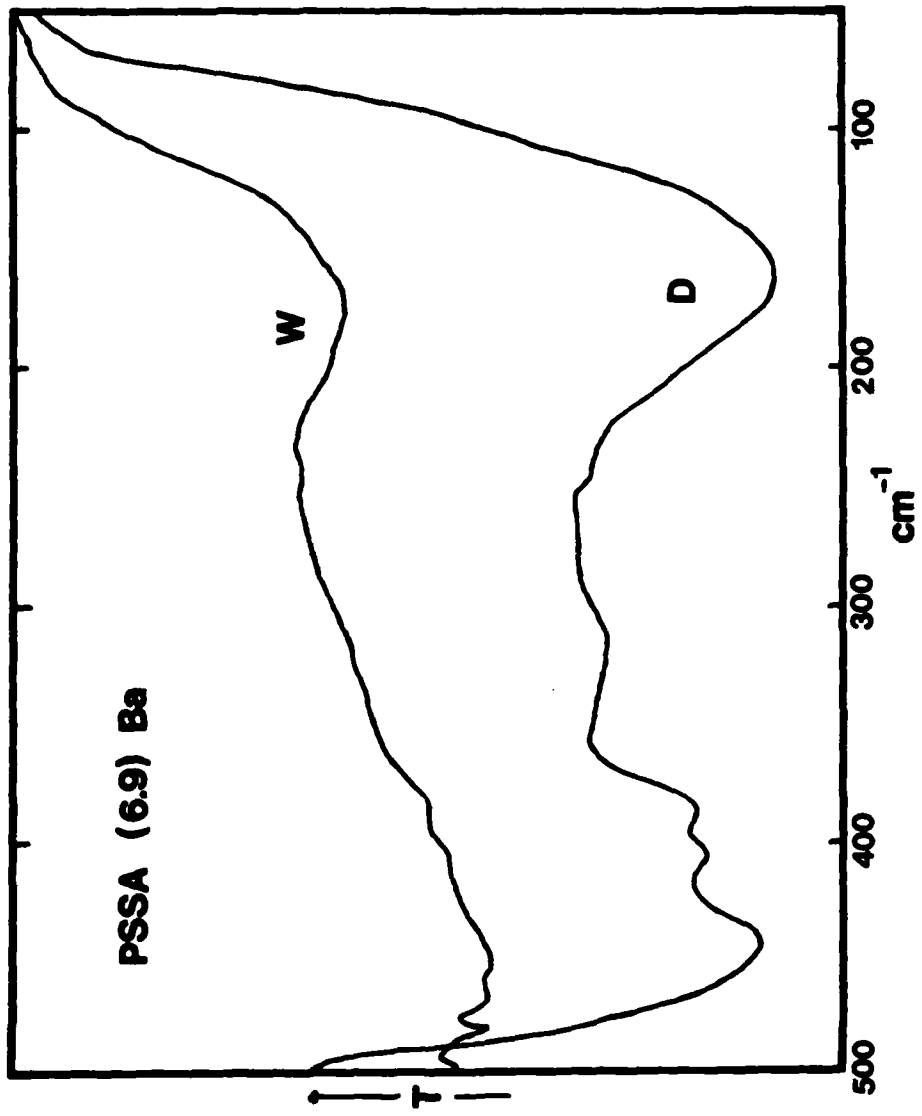
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28. The extent of dehydration at ca. 170°C and 1.5×10^{-2} torr for at least 4 days is determined by the ratio of the absorbance (A_{3400}) of the $\nu(\text{OH})$ infrared bands in the 3400-cm^{-1} region to the absorbance (A_{3029}) of the aromatic $\nu(\text{C-H})$ bands at 3029cm^{-1} . The level of hydration observed under these conditions corresponds to $I_{3400}/I_{3029} = 0(\pm 1\%)$ and applies to all spectra shown and referenced with this footnote.

Figure Captions

- Figure 1: Far infrared spectra of PSSA (6.9) Na, K, Rb and Cs dry (D) ionomer films (28).
- Figure 2: Far infrared spectra of PSSA (6.9) Ca, Sr and Ba dry (D) ionomer films (28).
- Figure 3: Far infrared spectra of a hydrated PSSA (6.9) Ba ionomer film (W) and of the same film after drying at ca. 170°C (D), (28).
- Figure 4: Far infrared spectra of a PSSA (16.7) Sr film which was first dehydrated at ca. 170°C (D), (28) and subsequently annealed at ca. 200°C for 24 hr. (A).
- Figure 5: Plots of the cation-motion frequency (ω) vs $(M_c + n)^{-1/2}$ for the dehydrated PSSA (6.9) Na, K, Rb, Cs, Ca, Sr and Ba films.
- Figure 6: A comparison of the far infrared spectra of PSSA (16.7) Ba films which are hydrated (W), dehydrated at ca. 170°C (D), (28), and annealed at ca. 200°C for 24 hr. (A).
- Figure 7: A comparison of the far infrared spectra of dehydrated (28) PSSA-Ba ionomer films with sulfonate compositions of 3.4, 6.9 and 16.7 mole percent.







PSSA (6.9) Ba

W

D

500 400 300 200 100 cm^{-1}

