

## INFRARED STUDIES OF IONOMER CLUSTERING

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### Summary

Cation-motion vibrational bands have been observed in the far infrared spectra of ionomers based on styrene-methacrylic acid copolymers, PSMA. The bands reflect the cation-site forces and state of aggregation. At low cation-site concentration the cation-motion band frequency varies with mass and charge of the cation. As the cation-site concentration increases, but the cation remains the same, a lower frequency band due to ion motion in higher order ion aggregates is observed. Since the anionic site vibrations do not change as the aggregate band appears, the low frequency reflects increased intercationic repulsions and an increase of vibrational reduced mass.

**Key words:** Infrared and Far Infrared Spectroscopy. Polymers. Ionomers. Ionic Interactions.

### Introduction

Ionomers are ion-containing polymers, generally copolymers, in which typically the ionizable  $H^+$  ions of acidic side groups are replaced by metal cations. They have been studied widely<sup>1-45</sup> and found to exhibit macroscopic properties which have led to important materials applications. Most studies have been performed on polymers prepared by copolymerizing an olefin, such as ethylene (E), butadiene (B), or styrene (S), with a carboxylic acid, such as acrylic acid (AA) or methacrylic acid (MA). This study concerns ionomers based on polystyrenemethacrylic acid (PSMA).

The copolymers on which ionomers are based tend to exhibit hydrogen-bonded association between physically adjacent carboxylic acid groups, and replacement of the  $H^+$  ions leads to formation of at least  $M^+-CO_2^-$  ion pairs. The possibility exists of forming higher order ionic domains as the concentration of ionic groups increases. The formation of such domains in ionomers can lead to microphase separation with a dispersed ionic phase too small to scatter visible light but large enough to significantly affect the mechanical and rheological properties of the materials. Such formation has been widely postulated to explain the composition dependence of these properties.

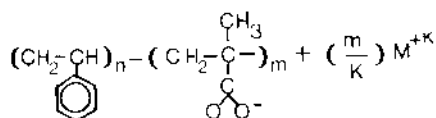
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Although there is general agreement that ionic polymers of this type feature a state of aggregation of ions and ionic sites dispersed in amorphous hydrocarbon-like media, several models have been proposed to describe the morphology of the ionomers and no direct observations of the postulated ionic domain have been reported. Based on our previous studies<sup>43-44</sup> of alkali metal ionomers of polyethylene methacrylic acid (PEMA), in which their far-infrared spectra were used to observe cation-motion vibrations, we have probed the cation-site interactions in several ionomers as a function of cation and ion-site concentration.

## Experimental

Polystyrene methacrylic acid (PSMA) ionomers, of the form below, where



$\text{M}^{+K}$  is  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$  or  $\text{Ba}^{+2}$ , were prepared by titrating (under nitrogen) 3-5% solutions of the acid (unionized) form of the PSMA copolymers<sup>12</sup> by standard solutions of the appropriate metal hydroxide in methanol to a phenolphthalein endpoint. For copolymers having an acid content greater than 1%, a 10% by volume solution of methanol in benzene was used as a solvent. The neutralized solutions were then freeze dried, vacuum dried at temperatures ca. 20°C above  $T_g$  and molded into films under pressure. The materials and their spectra are labelled by a number giving the concentration of the methacrylic acid comonomer in mole % followed by letters (H, Na, Li, Cs, Ba) in parentheses indicating acidic or metal neutralized copolymer, followed by a letter l or h indicating low (50,000-70,000) or high (ca 400,000) molecular weight respectively. For example, 4,6 (Na)h is the sodium-form ionomer of the PSMA copolymer in which 4.6 mole percent of the comonomer molecules are methacrylic acid and the molecular weight is about 400,000. Table I gives the acid concentrations of the samples studied in mole %, n/m ratio and in terms of carbon atoms between acid groups for the PSMA ionomers. The degree of replacement of carboxylic hydrogens by  $\text{M}^{+K}$  was 99-100% in the samples studied. This (Table I) can be ascertained from the mid infrared spectra of the ionomers.

TABLE I.

PSMA	Mole % acid	n/m	number of carbon atoms between acid groups
0.6	0.6	166	333
3.7	3.7	26	53
3.8	3.8	25	51
4.6	4.6	21	43
6.2	6.2	15	31
8.2	8.2	11	23

The films were compressed between two sheets of PTFE at 120°C in a stainless steel mold to obtain films of a suitable thickness for far infrared studies and annealed by cooling them in the mold at the rate of 1°/min before the infrared measurements were made. This heating and annealing was also done to relieve strain introduced during preparation and to remove residual surface water. Since the method of ionomer formation is a non-aqueous solution neutralization, little bulk water is expected to be present.

The far infrared spectra in the region 50-450  $\text{cm}^{-1}$  of 0.05-0.20 mm thick films of PSMA ionomers were recorded with a Digilab FTS-14 Fourier transform far infrared spectrometer at ambient temperature. Each spectrum was recorded several times with a reproducibility of 1% in absorbance. Mid infrared spectra in the region 600-3700  $\text{cm}^{-1}$  were recorded with a Digilab FTS-15B Fourier transform spectrometer and each trace represents the average of 64 scans completed in less than two minutes. All spectra were obtained with ca. 2  $\text{cm}^{-1}$  resolution.

Dehydration experiments were performed on the films prepared in the above manner and allowed to take up water from the atmosphere over a long period of time. The films were mounted on a brass support inside a specially designed variable temperature cell fitted with KBr windows. This cell permitted us to vary the temperature from 20° to 240°C continuously and to control and measure T within 1°C. The entire cell could be evacuated prior to or during the heating process. Spectra of a given film were taken at ambient temperatures, 70° and 130°-140°C and at various times during the dehydration process. The cell was always free of air and liberated water vapor due to continuous pumping through the evacuation port.

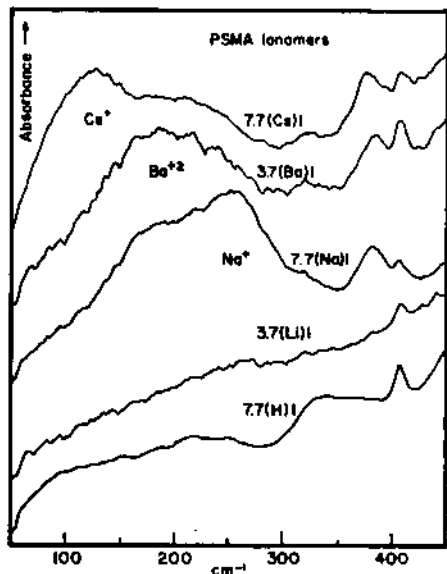


FIG. 1: Far infrared spectra (50-450  $\text{cm}^{-1}$ ) of low molecular weight PSMA ionomers and the unionized form of the low molecular weight copolymer.

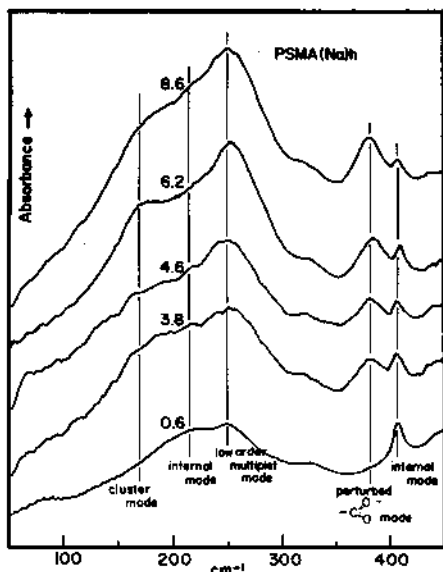


FIG. 2: Far infrared spectra spectra s a of high molecular weight PSMA - Na<sup>+</sup> ionomers with varying concentrations of carboxylic groups.

## Spectral Results

### a. Far Infrared Spectra

The far infrared spectra (50-450 cm<sup>-1</sup>) of the low molecular weight PSMA ionomers containing Cs<sup>+</sup>, Ba<sup>+2</sup>, Na<sup>+</sup>, and Li<sup>+</sup> and the un-ionized form of the low molecular weight copolymer are shown in Figure 1. A dominant feature appears in the Cs<sup>+</sup>, Ba<sup>+2</sup> and Na<sup>+</sup> ionomer spectra which is not present in the spectra of either the Li<sup>+</sup> ionomer or the un-ionized form in the region below 300 cm<sup>-1</sup>. This feature is a broad, well defined band which shifts from 250 ± 5 cm<sup>-1</sup> for the Na<sup>+</sup> ionomer to 185 ± 5 cm<sup>-1</sup> for Ba<sup>+2</sup>, to 115 ± 5 cm<sup>-1</sup> for Cs<sup>+</sup>. The frequency variation of these bands which are due to cation-site vibrations, is accounted for mainly by the changes in mass and charge of the cations. On this basis, the cation motion band in the Li<sup>+</sup> ionomer should appear in the 500 cm<sup>-1</sup> region, but the absorption due to other modes of the copolymer is too intense in that region of the spectrum for the Li<sup>+</sup> ion motion band to be observed. Since these bands shift strongly with cation mass charge, they are assigned to cation motion in the anionic field of the copolymer.

In Figure 2 are shown the spectra of a series of Na<sup>+</sup>-form PSMA ionomers in which the anionic-group (ionic) concentration is varied. As this concentration increases a band appears ca. 170 cm<sup>-1</sup> on the low frequency side of the main Na<sup>+</sup>-motion band. In the band structure observed between 150 and 300 cm<sup>-1</sup> there are three bands. The one at about 250 cm<sup>-1</sup> is the primary cation motion band and since it is present at low ionic concentration it is assigned to the vibration of an aggregate involving few ions (low order multiplet). The middle of the three bands at ca 220 cm<sup>-1</sup> is a weak internal mode of the polymer. The 170 cm<sup>-1</sup> band is assigned to the vibrations of aggregates involving many cations and anionic sites close together.

This is entirely consistent with the formation of higher aggregates or clusters, because the oscillations of cations in such ion domains should have both a larger effective mass and lower effective force field (since the cation-anion site attraction becomes increasingly screened). Thus, the vibrational frequency becomes lower than that of smaller cation-site oscillators, which is consistent with a previous observation<sup>45</sup> that in solution the ion motion frequencies for simple ion pairs is higher than that for higher aggregates.

Another important band appears at  $405\text{ cm}^{-1}$  in all the PSMA ionomer spectra. This band has approximately the same intensity in all the samples studied, after suitable corrections are made to account for varying sample thicknesses. This observation suggests that the band is due to a vibration along the polymer backbone which is independent of the ion content of the polymer. There are two reasonable assignments for this band. It may be assigned to an out-of-plane bend of the benzene ring, which is analogous to the one occurring at  $405\text{ cm}^{-1}$  in polystyrene. It could also be assigned to a C-C-C bend along the polymer backbone. In straight chain alkanes the C-C-C band is observed in the frequency range  $350\text{--}450\text{ cm}^{-1}$ .<sup>46</sup>

The constancy of the  $405\text{ cm}^{-1}$  band is significant in light of the appearance of another band observed in the  $400\text{ cm}^{-1}$  region, appearing at  $387\text{ cm}^{-1}$  in the  $\text{Li}^+$  ionomer,  $386\text{ cm}^{-1}$  in  $\text{Na}^+$ ,  $387\text{ cm}^{-1}$  in  $\text{Ba}^{+2}$ , and  $381\text{ cm}^{-1}$  in  $\text{Cs}^+$ . The fact that the band, which is absent in the acid form, shifts slightly to lower frequency as the cation mass increases and, more importantly, increases in intensity as the ion concentration increases (see Figure 2) suggests that the vibration giving rise to this band is associated with the anion site and is weakly dependent upon the nature of the cation. Two vibrational modes, clearly coupled, which meet this criteria are C-C-O and the O-C-O bending motions, both modes of the carboxylate group.

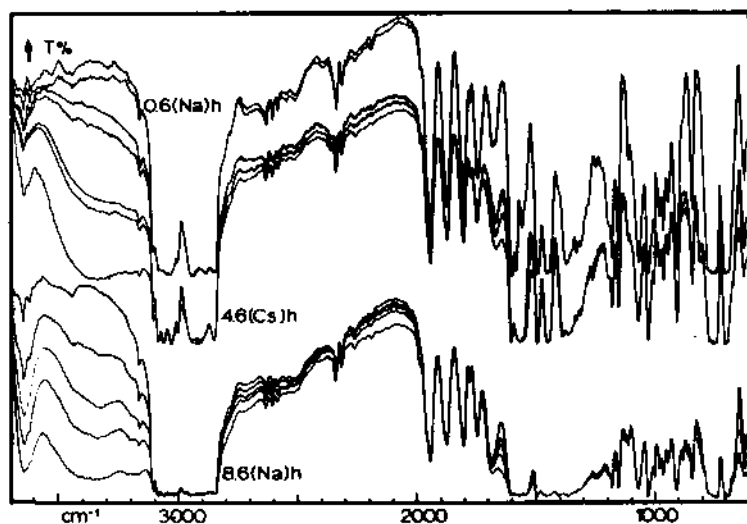


FIG. 3: Mid infrared spectra of some high molecular weight ionomers in hydrated, partially hydrated and dehydrated form.

### *b. Mid Infrared Spectra*

Several interesting features are seen in the mid infrared (Figure 3) spectra. The  $1700\text{ cm}^{-1}$  band which is characteristic of unionized  $-\text{COOH}$  groups is absent from all ionomer spectra. Instead a band in the  $1560\text{--}1570\text{ cm}^{-1}$  region is observed even in the case of low (0.6 mole %) ionic concentration. This band has been attributed<sup>11, 15</sup> to the asymmetric stretch of the  $-\text{COO}^-$  group while a weak band at  $1410\text{ cm}^{-1}$  corresponds to the symmetric stretch and is not easily observed. The  $1700\text{ cm}^{-1}$  band is distinctly present in the unionized copolymer spectra and the  $1560\text{ cm}^{-1}$  band is absent. This indicates that the ionomers were completely (99-100%) neutralized.

Dehydration of the ionomer films causes the suppression of the water bands in the  $3100\text{--}3700\text{ cm}^{-1}$  region (symmetric and asymmetric O-H stretch, the  $1650\text{ cm}^{-1}$  region (water bending vibration), and the ca.  $650\text{ cm}^{-1}$  region (torsional vibrations). Otherwise the spectra of the ionomer films do not change significantly even when heated to  $130^\circ\text{--}140^\circ\text{C}$ .

Moreover, we have found that films with a high mole percent of ionic groups tend to take up much more water than films with a low percentage of ionic groups. This is consistent with Eisenberg's observations that below 6 mole per cent the uptake of water is ca 1 molecule per carboxylic group, whereas, at higher ionic concentrations, it is between 3-6 molecules per carboxylic group.

### Discussion

It is clear from the interpretation of the far infrared data that as the concentration of ionic sites increases the cation finds itself in more than one kind of environment. If at very low ionic site concentrations the sodium ion and the carboxylate ion form low order multiplets involving 1-4 cations plus anionic sites, the vibration of the cations in the force field of the anions and the hydrocarbon backbone give rise to the band at ca  $250\text{ cm}^{-1}$ . With increasing ionic concentration, and much the same way as occurs in solution, higher aggregates are formed.

Whether the higher order aggregate band at  $170\text{ cm}^{-1}$  should be assigned to vibrating clusters<sup>48</sup> or «ion drops», as defined by Holliday<sup>47</sup> or other specific higher order aggregates cannot be asserted from our results. This is true despite the fact that it might be attractive to assign the  $170\text{ cm}^{-1}$  band to vibrating ion drops because it is observed even for low (3.8 and 4.6 mole %) ion concentrations. Rheological, small angle X-ray scattering and time-temperature superposition evidence for clustering is apparent at ionic concentrations greater than 6 mole per cent for PSMA ionomers. However, our spectroscopic method may be more sensitive in detecting the existence of clusters than the above techniques and it detects them as they form and increase in concentration even before they become important rheologically.

Within the vibrating higher order aggregate repulsions between mobile cations tend to alter the force field felt by the cation and cause low frequency ion motion vibrations. Interactions between cations adjacent to the carboxylate sites and these sites themselves are not greatly affected by this aggregation since the carboxylate band in the  $400\text{ cm}^{-1}$  region is not shifted.

The principal driving force for the formation of ion aggregates is the low dielectric constant of the backbone since the interionic attraction per cation changes little as aggregation proceeds. Whenever distances between ions are small enough, this driving force causes higher aggregates to be formed. The spectroscopic

evidence, therefore, is consistent with the proposition<sup>49</sup> that at low ionic concentrations small ion aggregates are formed, but at higher concentrations clustering of such aggregates to form ionic domains predominates.

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## Περίληψη

### Υπερύθρη Μελέτη Συσσωματώσεως σέ Ίονομερή

Παρατηρήσαμε ταινίες που όφείλονται στην ταλάντωση του κατιόντος στο άνω υπέρυθρο φάσμα Ίονομερών, παρασκευασμένων από προϊόντα συμπολυμερισμού στυρολίου και μεθακρυλικού όξέος. Οί ταινίες αυτές αντικατοπτρίζουν τις δυνάμεις μεταξύ κατιόντος και γειτονικών ομάδων και μία κατάσταση συσσωματώσεως ιοντικών ομάδων ή σωματιδίων μέσα στη πολυμερική μήτρα. Για χαμηλές συγκεντρώσεις ιοντικών ομάδων στο Ίονομερές, ή συχνότητα της ταινίας που όφείλεται στη δόνηση του κατιόντος μεταβάλλεται με την μάζα και τδ φορτίο του κατιόντος. Ίονομερή του ίδιου κατιόντος, αλλά με αύξημένη συγκεντρωση ιοντικών ομάδων, εμφανίζουν μία νέα ταινία χαμηλής συχνότητας που όφείλεται στην δόνηση κατιόντων σ' ένα μεγαλύτερο ιοντικό σύμπλεγμα (πλειάδα ή ιοντική σταγόνα). Έπειδή οί ταλαντώσεις της άνιοντικής ομάδας δέν μεταβάλλονται με την εμφάνιση της ταινίας αυτής, συμπεραίνομε ότι ή χαμηλή συχνότητα της ταινίας της πλειάδας αντιπροσωπεύει αύξημένες άπίψεις μεταξύ κατιόντων και μεγαλύτερη άνηγγμένη μάζα του δονουμένου ιοντικού συμπλέγματος.

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- 48 The term «cluster» implies ion-rich regions alternating with ion-poor regions. MacKnight<sup>25</sup> *et al.* has proposed a model consisting of a large central multiplet (ionic region) coated with a non ionic skin and surrounded by other multiplets or ion pairs. Eisenberg's model is that of a collection of interacting multiplets separated by non-ionic material. See: Eisenberg, A. and King, M., in *Polymer Physics*, Vol 2. «*Ion Containing Polymers*», Stein, R.S. editor, Academic Press, Inc. New York, 1977.
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