

Ionomers: Two Formation Mechanisms and Models

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SYNOPSIS

The FT IR spectra for different degrees of neutralization of ionomers based on poly(ethylene-methacrylic acid) copolymer were obtained. They involve the alkali metal ions (such as lithium, sodium, potassium, rubidium, and cesium), the alkaline earth metal ions (such as magnesium, calcium, strontium, and barium), and the transition metal ions (zinc and copper). Through the analysis of these spectra it can be deduced that there are two formation mechanisms and corresponding models for the ionomers: a cluster-multiplet model and a coordinated complex model. Also, it can be seen that the metal cations play an important role in the structure of an ionomer. By comparing the spectra of the metal ionomers at different temperatures as well as the spectra of the metal ionomers before and after water immersion, the existence of the two formation mechanisms and models can be inferred further.

INTRODUCTION

Eisenberg proposed the multiplet-cluster model.¹ Various publications have supported this concept. The studies were based on far-infrared spectra,² transmission electron microscopy (TEM),³ Raman spectra,⁴ annealing results,⁵ FT IR spectra,⁶ and theoretical analysis.⁷ Some authors did not agree with this kind of model. They did not find ionic clusters,⁸ a low-frequency Raman spectroscopic study⁹ of the ionomer cannot be associated unambiguously with structures such as "clusters" or "multiplets," theoretical studies¹⁰ do not support Eisenberg's distinction between multiplets and clusters but simply define ionic aggregates as "clusters," and FT IR studies¹¹ led to the proposal of possible structures for multiplets with coordination numbers of 4, 6, and 8. The investigation of ESR spectra¹² of ethylene-acrylic acid copolymers neutralized with manganese acetate indicated that the structure of the Mn(II) salts may be a bridging structure. The result¹³ of a small-angle X-ray (SAXS) study of Mn-SPS (sulfonated atactic polystyrene) indicated the absence of microphase-separated ion-rich clusters in the as-cast ionomer.

Therefore, major questions concerning the state of ion aggregation still remained open. Whether there are multiplets and clusters in the ionomers was still in dispute.

It was considered possible to study the existence of multiplets and clusters through an understanding of the processes of ionomer formation. In this article the FT IR spectra of different degrees of neutralization of ionomers based on ethylene-methacrylic acid copolymer are shown. They included Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Cu, and Zn ions, respectively. Through the analysis of these spectra it is proposed that there are two formation mechanisms and models for ionomers. One is multiplet-cluster model that is suitable for alkali and alkaline earth metals. The other is a specific coordinated complex model that is suitable for the transition metal ionomers such as those of zinc and copper. In order to prove these suggestions, the comparisons of the spectra of each metal ionomer at room temperature and at 70°C as well as the spectra of each metal ionomer before and after water immersion are also used from the literature.

EXPERIMENTAL

Preparation of Poly(Ethylene-co-methacrylic Acid) from Surlyn 1650

Surlyn 1650 was obtained from Du Pont. It is an ionomer based on poly(ethylene-co-methacrylic

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acid) neutralized with sodium and zinc ions and reported to contain 4.1 mol % methacrylic acid.

Surlyn pellets were finely ground in a grinder (C. W. Brabender Instruments Inc.), then refluxed in tetrahydrofuran with 1*N* hydrochloric acid for 24 h to produce the completely unneutralized copolymer. The acid form was then precipitated with cold methanol-deionized water (1 : 1), filtered, washed with more methanol-deionized water mixture, and then freeze-dried at -50°C for more than 24 h. The purity of the poly(ethylene-co-methacrylic acid) was checked by its infrared spectrum (Fig. 1), which agreed with the standard spectrum.¹⁴

Preparation of Metal Ion Salts of Ethylene-Methacrylic Acid Copolymer

The ethylene-co-methacrylic acid copolymer was refluxed with tetrahydrofuran with or without a little deionized water depending on the desired reaction rate.¹⁵ Different metal hydroxides were used to neutralize the methacrylic acid in order to obtain the metal ionomers. Samples with various degrees of neutralization were collected during the process of the chemical reactions. Each sample was precipitated in cold methanol-deionized water, then filtered, washed several times with more methanol, and freeze-dried at -50°C for more than 24 h.

Film Preparation

To prepare a film for infrared measurement, each sample was pressed in a laboratory press using a mold at different temperatures depending on the ionomer (according to experience) and under 24,000

psi for several minutes. These films were thin enough to be within the range in which Beer's law is obeyed.¹⁶

After each pressing, the mold with the film sample was quenched in liquid nitrogen in a desiccator over anhydrous CaSO_4 to avoid moisture. The films were stored at room temperature in the desiccator over silica gel or anhydrous CaSO_4 prior to infrared spectral measurements. The films should be completely relaxed and isotropic.

Determination of the Degree of Neutralization

All samples were measured on a Nicolet 60sx FT IR spectrometer. The spectrum was scanned between 1400 and 1800 cm^{-1} with a resolution of 4 cm^{-1} . The spectra were stored on a magnetic disk. The degree of neutralization of each sample was obtained by the FT IR method.¹⁵

High-Temperature Spectra

The copper ionomer spectrum at 70°C was measured by using a high-temperature cell with a temperature controller. The other comparison spectra for each metal ionomer at room temperature and 70°C as well as the spectra of water-immersed samples of ionomers were unpublished data from the thesis of Brozoski.

RESULTS AND DISCUSSIONS

In principle, vibrational spectroscopy should be an excellent technique with which to study these complex multiphase system. The work done by Painter⁶ and Rouse² and their co-workers demonstrated that vibration spectroscopy is potentially a powerful tool for investigating the structure of ionomers. The spectroscopic method may be more sensitive than some other techniques for indicating the existence of clusters and multiplets. For studying the formation mechanisms of ionomers, the FT IR spectra of different metal ionomers from a low degree of neutralization to a higher degree (or complete) neutralization were investigated. These ionomers included those of alkali metal ions, the alkaline earth metal ions, and two typical transition metal ions. These spectra are shown in Figures 2–12.

By comparing the unneutralized copolymer and alkali, alkaline earth, and transitional metal ionomers, the following can be observed:

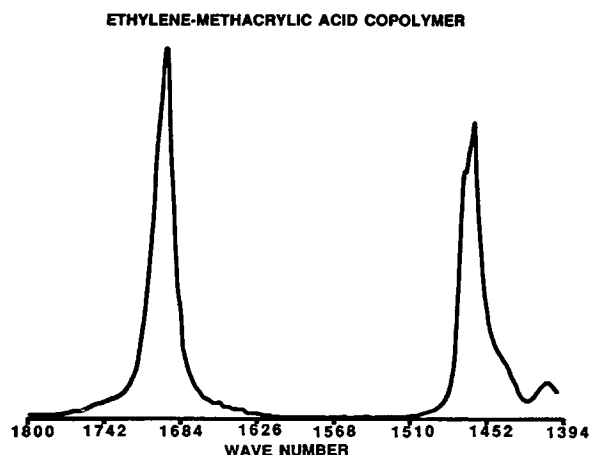


Figure 1 Infrared spectrum of poly(ethylene-co-methacrylic acid).

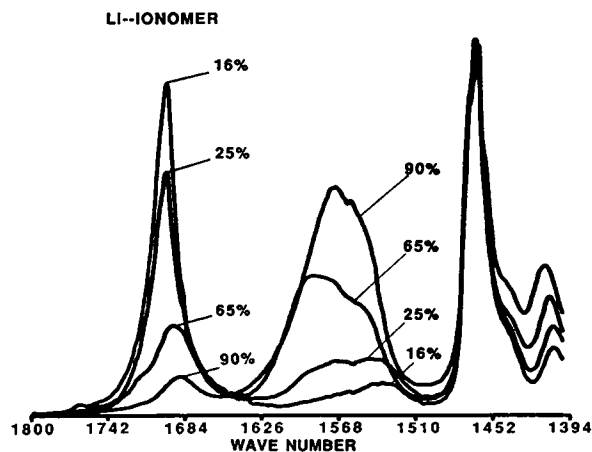


Figure 2 FT IR spectra in the $1400\text{--}1800\text{ cm}^{-1}$ range of the lithium ionomer at varying degrees of neutralization.

1. As the degree of neutralization increased, the peaks for the 1698-cm^{-1} carbonyl group vibration for all alkali and alkaline earth metal ionomers were changed. Not only were the absorption intensities reduced but also the peak wave numbers were shifted to a lower wave number (Fig. 13). Also, it can be seen that the wave number shifts are greater for the alkaline earth metal ionomers than those for the alkali metal ionomers. No such changes appeared for the transition metal ionomers.
2. New peaks that did not appear in the raw copolymer appeared in the region about $1480\text{--}1670\text{ cm}^{-1}$ for all alkali, alkaline earth, and transition metal ionomers. But the features

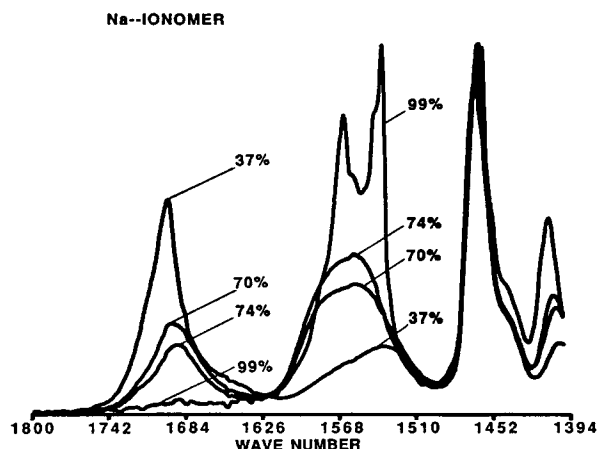


Figure 3 FT IR spectra in the $1400\text{--}1800\text{ cm}^{-1}$ range of the sodium ionomer at varying degrees of neutralization.

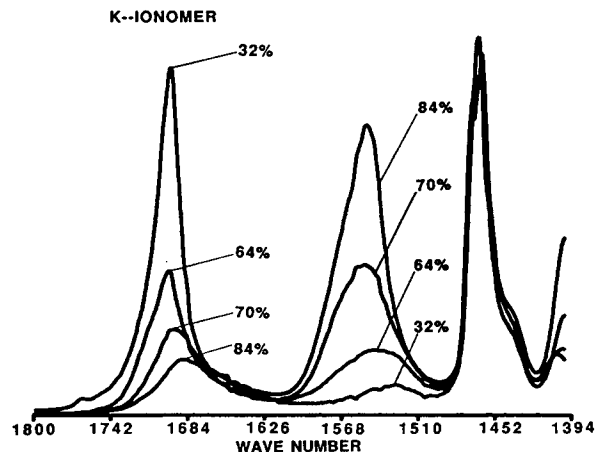


Figure 4 FT IR spectra in the $1400\text{--}1800\text{ cm}^{-1}$ range of the potassium ionomer at varying degrees of neutralization.

of these new peaks differed. As the degree of neutralization changes, the phenomena of peak shifting and band broadening appeared in all alkali and alkaline earth metal ionomers (Fig. 14). No peak shift or band broadening appeared in this region for the transition metal ionomers.

These phenomena suggest that there are two mechanisms of ionomer formations, the multiplet-cluster mechanism for alkali and alkaline earth metal ionomers and a specific coordinated complex mechanism for transition metals such as zinc and copper. Even in the multiplet-cluster formation mechanism, there still exist differences between alkali and alkaline earth metal ionomers. Therefore,

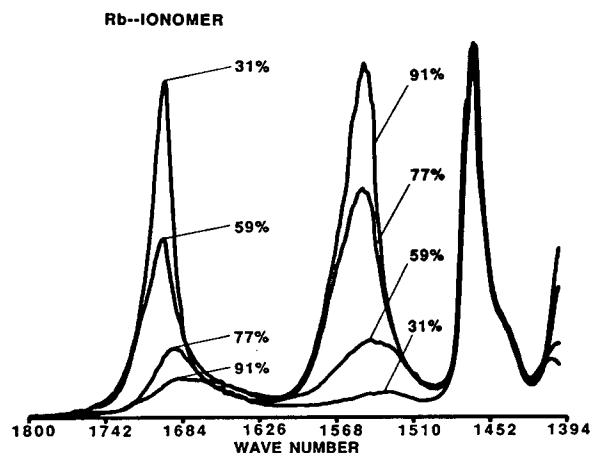


Figure 5 FT IR spectra in the $1400\text{--}1800\text{ cm}^{-1}$ range of the rubidium ionomer at varying degrees of neutralization.

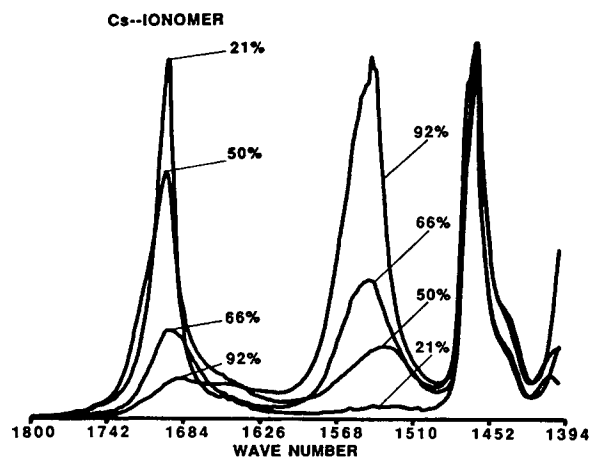


Figure 6 FT IR spectra in the 1400–1800 cm^{-1} range of the cesium ionomer at varying degrees of neutralization.

it seems that it is impossible to use a single model to cover all ionomer structures.

I. MULTIPLY-CLUSTER FORMATION MECHANISM

Common Characteristics for Alkali and Alkaline Earth Metal Ionomers

With increasing degrees of neutralization, the peaks for the carbonyl group in the 1698- cm^{-1} region are shifted. The reason has been described.¹⁵ Only a brief interpretation is given here. The basic idea is the existence of multiplets and clusters. These multi-

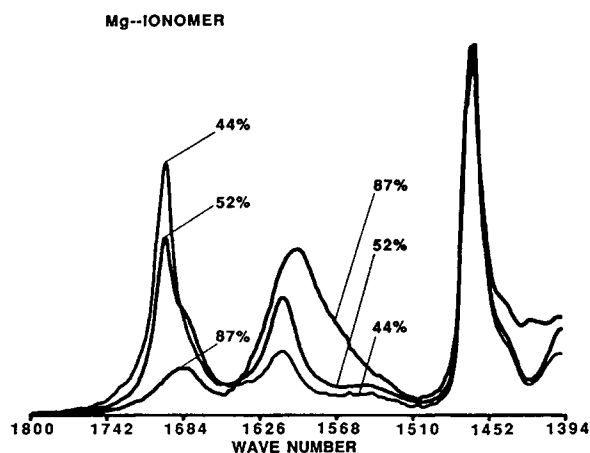


Figure 7 FT IR spectra in the 1400–1800 cm^{-1} range of the magnesium ionomer at varying degrees of neutralization.

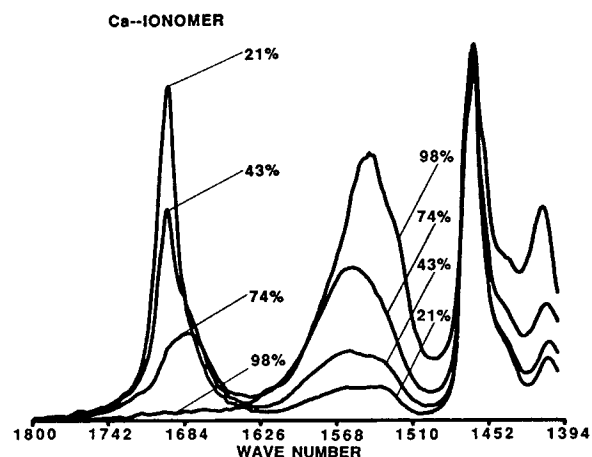


Figure 8 FT IR spectra in the 1400–1800 cm^{-1} range of the calcium ionomer at varying degrees of neutralization.

plets and clusters form a local polar environment. They possess the ability to accept electrons because clusters and multiplets involve metal cations. The unneutralized carboxyl groups are basic (electron donors), and they extend to complex with the acid (electron acceptors). The higher the degree of neutralization the stronger the acid so that as the degree of neutralization increases the acid groups will gradually become sufficiently strong to form significant acid-base complexes. Thus the phenomenon of the acid-base shifts of the infrared absorption peaks in ionomers can be explained. The existence of multiplets and clusters can be deduced from the shifts of the peak absorptions of the carbonyl groups in the 1698- cm^{-1} region for alkali and alkaline earth metal ionomers.

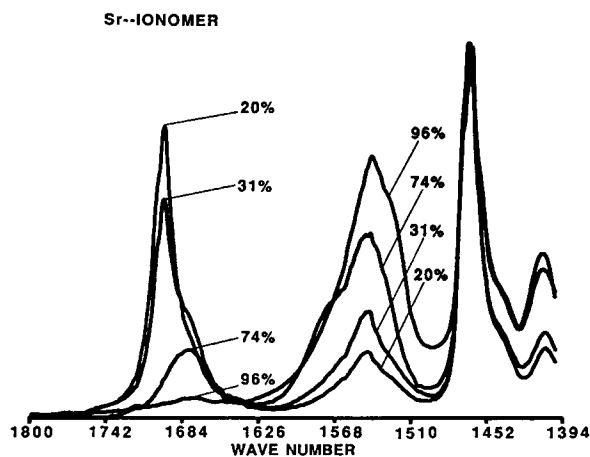


Figure 9 FT IR spectra in the 1400–1800 cm^{-1} range of the strontium ionomer at varying degrees of neutralization.

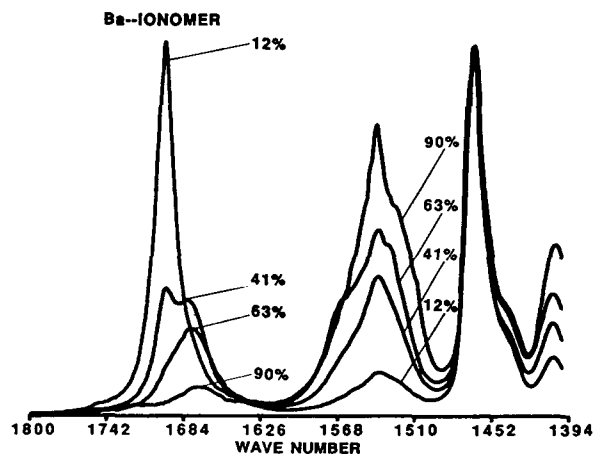


Figure 10 FT IR spectra in the 1400–1800 cm^{-1} range of the barium ionomer at varying degrees of neutralization.

There are several chemical equilibria during cluster formation. Also there are some differences in the formation mechanisms between the alkali and alkaline earth metal ionomers.

Formation Processes of Alkali and Alkaline Earth Metal Ionomers

Alkali Metal Ionomers

From Figures 2–6 and 14 it can be seen that the new carboxylate peak shifts to a higher wave number, and the peak shape changes from wide to narrow as the degree of neutralization increases. These phenomena can be interpreted by multiplet and cluster formation.

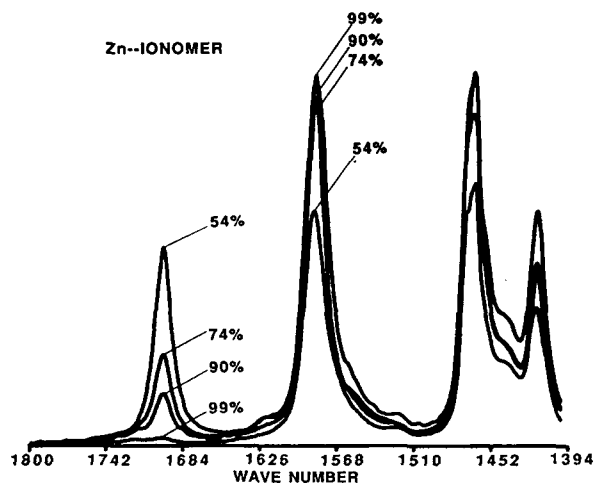


Figure 11 FT IR spectra in the 1400–1800 cm^{-1} range of the zinc ionomer at varying degrees of neutralization.

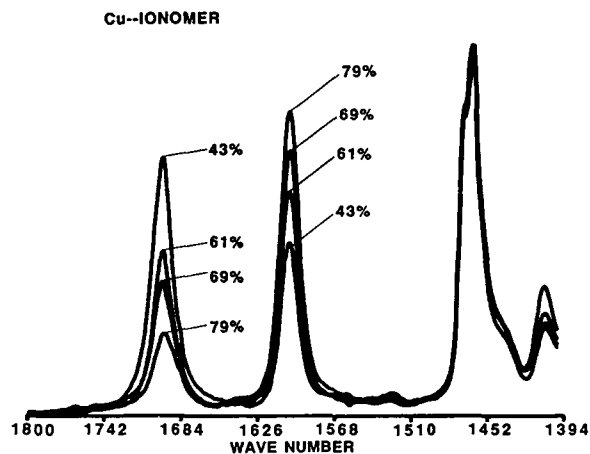


Figure 12 FT IR spectra in the 1400–1800 cm^{-1} range of the copper ionomer at varying degrees of neutralization.

With the neutralization reaction proceeding, more and more carboxylate groups are produced. They are polar groups that will be aggregated as

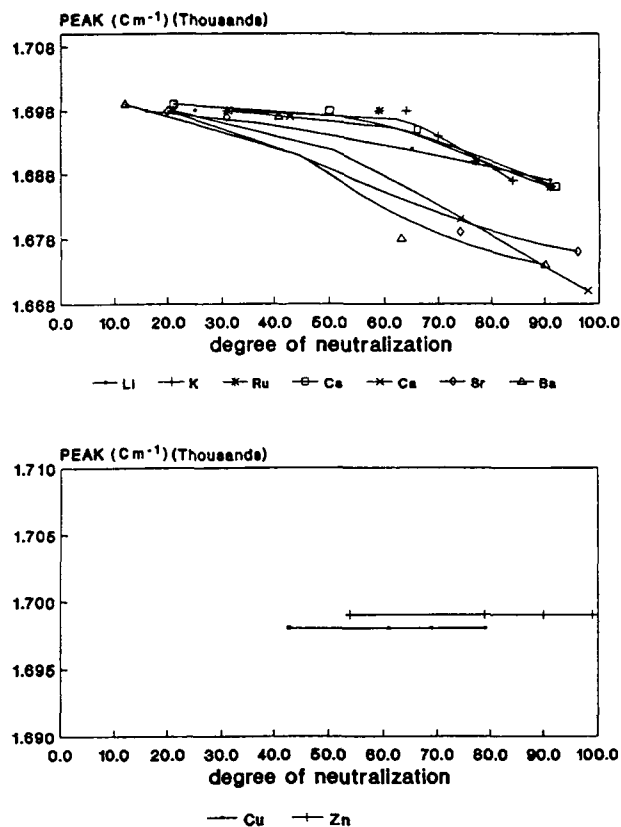


Figure 13 The peak shifts of alkali, alkaline earth, and transition metal (zinc and copper) ionomers of FT IR spectra in the region of 1698 cm^{-1} (peak wave number vs. degree of neutralization).

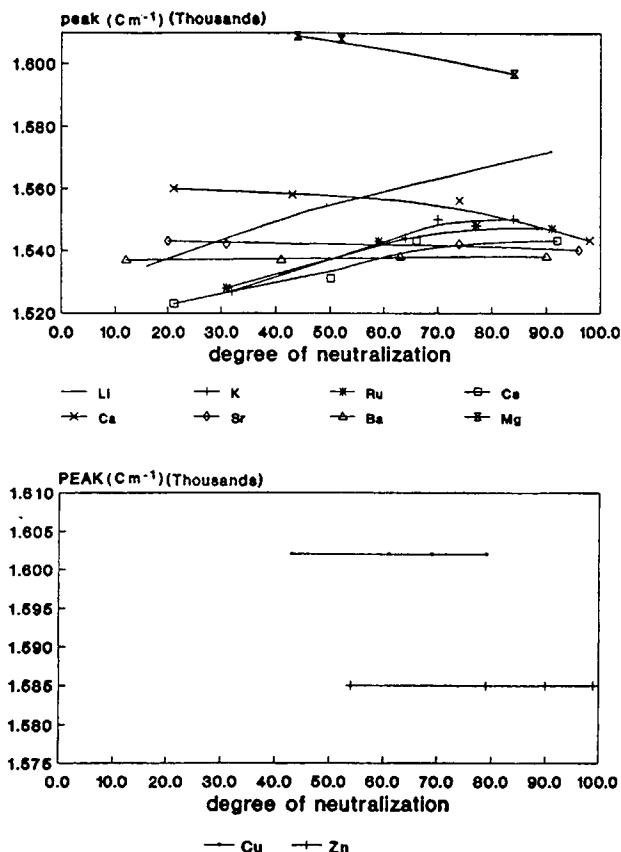
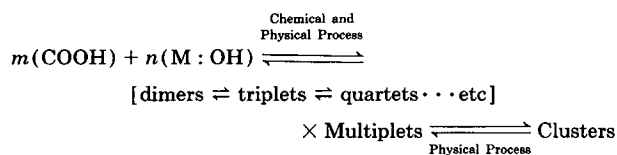


Figure 14 The peak shifts of alkali, alkaline earth, and transition metals (zinc and copper) ionomers of FT IR spectra in the 1480–1670 cm^{-1} region (peak wave number vs. degree of neutralization).

closely to each other as is physically possible resulting in electrostatic forces.¹ The number of ion pairs involved in aggregation will be increased gradually with increasing degree of neutralization. Meanwhile, several chemical equilibria are established. The process of cluster formation can be shown schematically as follows:



According to Eisenberg's work,¹ the basic ionic pair consists of one anion (the acid) and a neutralizing charge (the cation). The main driving force is electrostatic. With the degree of neutralization increasing, the concentration of carboxylate groups increases, and the chemical equilibrium tends toward the right. It means that the dominative associative forms would be gradually changed from ion pairs to

triplets to quartets, etc. until multiplets are formed. But the size of a multiplet is limited by steric hindrance and other factors.¹ Once the multiplet has been formed, it is completely coated by neutral material. These multiplets can be considered as a ionic drop in which the ion pairs might act as dipoles. As a result of these dipoles being attracted to each other (dipolar forces), the clusters are favored.

According to the basic equations of infrared spectroscopy,¹⁷ there is a relationship between the wave number of the absorption peak and the vibrations of bonds in the molecules.

$$\sigma = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}} \quad (1)$$

where σ is the wave number of absorption peak (cm^{-1}), K is the force constant of the bond (dynes/cm), C is the velocity of light (3×10^{10} cm/s), and m_1, m_2 is the masses of the atoms 1 and 2 (g). This equation shows that the wave number of the absorption peak is proportional to the force constant of the bond. Supposing this equation can be roughly applied to macromolecular analysis, the phenomena previously mentioned can be explained.

At the low degrees of neutralization the concentrations of carboxylate groups are not high enough; the ion pairs form small aggregations like dimers or triplets, etc. The crosslinking bonds involved in the small aggregations are fewer than those involved in the large ion pair aggregation. The more crosslinking bonds, the stronger the force constant of the bond, and the greater the wave number. Thus the wave number for the small aggregations of ion pairs is lower than that for the large aggregations of ion pairs. This means that the wave number for dimer, triplets, quartets, etc. would be changed to a higher value gradually. At any degree of neutralization, that is at any equilibrium state, there is always a certain ion pair aggregation form which would predominate. Therefore at each degree of neutralization there is always a dominant peak. This does not exclude the existence of other aggregation forms, which involve different numbers of ion pairs, but these aggregation forms are not dominant.

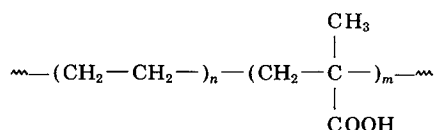
Consequently, with the degree of neutralization increasing, the concentration of carboxylate groups increases, the dominant aggregation form changes from dimer, to triplet, to quartet, etc., to multiplet, and finally to cluster. The peak wave number will shift to a higher value. At the same time, owing to the existence of other kinds of aggregation, wave number overlap appears, the peak shape changes

from broader at the low degree of neutralization to narrow at the higher degree of neutralization.

Alkaline Earth Metal Ionomers

By comparing spectra of alkali and alkaline earth metal ionomers shown in Figures 2-6, 7-10, and 14, it can be seen that there are two different features about the peaks in the region of $1480\text{--}1670\text{ cm}^{-1}$. One is that at the lower degree of neutralization the peak shape of the alkali metal ionomers is broader than that for alkaline earth metal ionomers. The other is that for the same kind of ionomer with increasing degree of neutralization the peaks of the alkali metal ionomers shift to larger wave numbers whereas the peaks of the alkaline earth metal ionomers shift to smaller wave number. This phenomenon can be interpreted as follows.

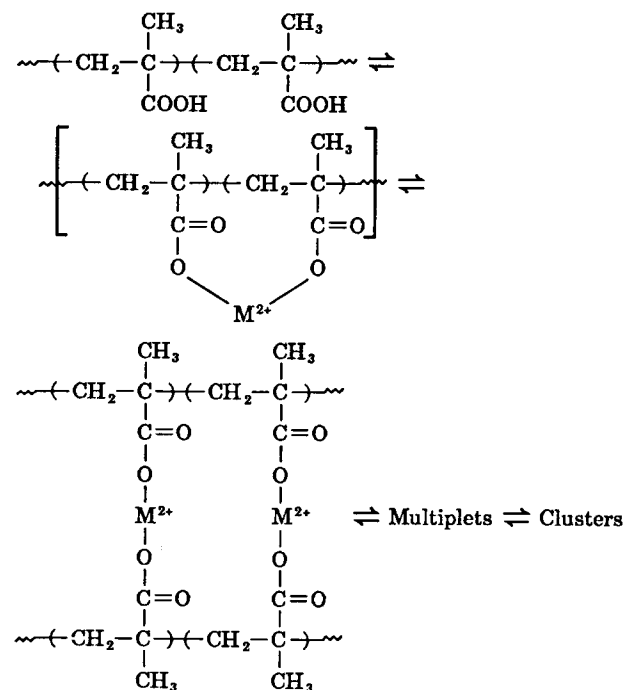
Suppose that ring structures are formed at the lower degrees of neutralization for alkaline earth metal ionomers. The structure of ethylene-methacrylic acid copolymer would be represented schematically as follows:



The methacrylic acid content of the copolymer is 4.1 mol % for a random distribution of methacrylic acid groups. This would yield an average value of n of about 25 for $m = 1$. However, according to MacKnight's results,¹⁸ there may be some tendency for the methacrylic acid units to exist in blocks ($m > 1$). In order to control the rate of neutralization, low concentrations of the copolymer solution were chosen (below 1%). Therefore, at the beginning of the neutralization reaction, because the distance between two macromolecules is too great, it may be easier for the divalent cation to form eight-member rings between two neighboring methacrylic acid groups than to form bonds between two macromolecules.

As the reaction proceeds, the methacrylic acid groups that have neighboring methacrylic acid groups become fewer, and neutralization reaction has to proceed between two macromolecules. Thus more and more bonds appear between two macromolecules, which will reduce the distance between two macromolecules and increase the contacts between them. From the energetic point of view the eight-member rings are less stable than single bonds. Finally, the eight-member rings open and single

bonds form between two macromolecules. Ultimately multiplets and clusters are formed. The latter process is similar to the formation of multiplets and clusters for alkali metal ionomers. This process may be represented schematically as follows:



Since the eight-member rings include more bonds, the force constant of an eight-member ring would be larger than that of the intramolecular bonds. Thus the wave number for rings would be larger than that for intramolecular bonds. Therefore, the peak wave number at lower degrees of neutralization (ring forms) is higher than that at the higher degree of neutralization. The peak shape seems sharper compared to those of alkali metal ionomers because these peaks are representative of eight-member ring vibrations. The peak wave number will be shifted at a degree of neutralization at which the rings start to be opened.

As the degree of neutralization increases, clusters and multiplets are formed. The peak wave number will shift toward a smaller value. In the latter process there still exists equilibria between clusters and multiplets, so that the peaks of both clusters and multiplets can be seen.

Relationship between Ionomer Structures and Cations

It was assumed that there are cluster-multiplet structures during alkali or alkaline earth metal ionomer formation and the main driving force is elec-

trostatic. Thus some relationship between cluster-multiplet structures and the properties of cations should be found.

From Figure 13 and Table I it can be seen that the peak shift values of the carbonyl groups (in the 1698-cm⁻¹ region) are smaller for alkali ionomers than for alkaline earth metal ionomers and the shift values increase with the cation type from top to bottom in the same group of metals.

From Figure 14 and Table I it can be seen that for the carboxylate groups (in the 1480–1670 cm⁻¹), all alkali metal ionomers have the same peak shift trend and all the alkaline earth metal ionomers have a different peak shift trend. The peak shift values are toward smaller values as the cation radius becomes larger in the same group of metals. These phenomena reflect the influences of the metal cations on the ionomer structures.

The peak shifts of the carbonyl groups were produced by the local polar environments mentioned previously.

According to the results of Fowkes et al.¹⁹ the acid–base shift ($\Delta\nu^{ab}$) is directly proportional to the enthalpy of acid–base interaction (ΔH^{ab}), that is

$$(\Delta\nu^{ab}) \propto (\Delta H^{ab})$$

The empirical correlation about the enthalpy of adduct formation is represented by the equation as follows:

$$-\Delta H = C_a C_b + E_a E_b \quad (2)$$

where E_a and C_a are measures of the acid strengths and E_b and C_b are measures of the basic strengths. In our system the base strength ($-\text{COO}^-$) group does not change with different ionomers; the acid strength varies from ionomer to ionomer. As the cations involved in ionomers are changed from Li^+ to Cs^+ or from Mg^{2+} to Ba^{2+} , the acid strengths increase, therefore, the value of the enthalpy changes from small to large, and the shift value for the carbonyl groups changes to greater values.

In general the environmental electrostatic strength is stronger for divalent ions than for monovalent ions so that the shift values of divalent metal ionomers are greater than those of monovalent metal ionomers.

With increasing degrees of neutralization, the peak shift values of carboxylate group in the 1480–1670 cm⁻¹ region are different for different ionomers. These phenomena are caused by the ionomer structures themselves.

According to Eisenberg's theory, in media of low dielectric constant the ions would exist at least as

contact ion pairs (or even as higher multiplets). The interaction energy per ion pair is larger than the interaction of ion pairs existing as separated ions (no steric effects are involved in ion pair formation) so ion pairs are formed.¹

When the ion pairs gradually aggregate to form a cluster, the peak wave number gradually shifts from a low to a higher value. According to Eisenberg's theory, the average number of ion pairs involved in a cluster can be expressed as follows:

$$n = \frac{\rho N_{Av}}{M_0} \left[\frac{4l^2}{3kT_0} \frac{\bar{h}^2}{h_0^2} \frac{M_0}{M_0} \frac{k'}{K} \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} + 2 \left(\frac{n_0 M_0}{\rho N_{Av}} \right)^{2/3} \right]^{3/2} \quad (3)$$

where k' is the ($=W'/W$), dimensionless geometry-dependent factor giving the magnitude of the electrostatic energy released per ion pair in cluster formation, n_0 is the average number of ions pairs in multiplet, n is the average number of ion pairs in cluster, r is the distance between centers of charge in ion pair, and e is the electron charge, and the other symbol meanings can also be found in Ref. 1. For alkali and alkaline earth metal ionomers, only n_0 , r , e , and k' differ from each other. The other parameters are basically the same for the same group cation ionomers because these are made from the same raw copolymer, and they are made by similar procedures.

Comparing ionomers of the same metal group, the formation mechanisms are the same. These ionomers have the same geometric features so that the dimensionless geometry-dependent factor, k' , is supposed to be the same, and their electrical charge, e , is the same. Only n_0 and r change as the radius of the metal ions changes.

The total number of ion pairs in the multiplet (n_0)¹ can be expressed as the ratio of the volume of the multiplet (V_m) to the volume of an ion pair (V_p), as in

$$n_0 = V_m / V_p \quad (4)$$

As the radius of the metal ion increases, the volume of a multiplet (V_m) will be decreased. The reason is as follows. In the region of low ion concentration the ions are assumed to exist in the form of simple ion pairs. The ease with which these would form multiplets should be a function of the interior distance in such a multiplet.²⁰ The larger the interior distance, the smaller the energy required to remove an ion pair and the fewer the ion pairs kept in the multiplet. Therefore, V_m will be smaller. As the radius of the metal ion increases, the ion pair volume

Table I The Relationship between the Metal Ion Radius and the Peak Shift of the FTIR Spectra

Element Radium*	Degree of Neutralition	Peak Region (cm ⁻¹)			
		At 1700	Shift Value	At 1480–1670	Shift Value
Li	16	1698		1535	
(60)	25	1698	11	1545	37
60	65	1692		1586	
	90	1687		1572	
Na	37	1698		1535	
(95)	70	1694	7	1556	
95	74	1691		1557	32
	99			1567	
K	32	1698		1527	
(133)	64	1698	11	1544	23
133	70	1694		1550	
	84	1687		1550	
Rb	31	1698		1528	
(148)	59	1698	12	1543	19
148	77	1690		1548	
	91	1686		1547	
Cs	21	1699		1523	
(169)	50	1698	13	1531	20
169	66	1695		1543	
	92	1686		1543	
Mg	44	1698		1609	
65	52	1698	12	1608	12
(82)	87	1686		1597	
Ca	21	1698		1560	
99	43	1697	28	1558	17
(118)	74	1681		1556	
	98	1670		1543	
Sr	20	1698		1543	
113	31	1697	22	1542	3
(132)	74	1679		1542	
	96	1676		1540	
Ba	12	1699		1537	
135	41	1681	25	1537	1
(153)	63	1678		1538	
	90	1674		1538	
Cu	43	1698		1602	
96	61	1698		1602	
(96)	69	1698		1602	
	79	1698		1602	
Zn	54	1698		1585	
74	74	1699		1585	
(88)	90	1699		1585	
	99	1699		1585	

* Values (in pm) of Pauling crystal radii and (in parentheses) univalent radii of ions (Ref. 21, p. 70).

(V_p) increases obviously, so that the average number of ion pairs involved in a multiplet (n_0) becomes smaller [Eq. (4)]. Therefore the ion pairs involved in a multiplet of Li-ionomer are more than those involved in Cs-ionomer. The same results can be deduced for alkaline earth metal ionomers, i.e., more ion pairs are involved in the multiplet of Mg-ionomer than in the Ba-ionomer.

Consequently, as the radius of the metal ion changes to larger values according to Eq. (4) and (3), the average number of ion pairs in the multiplet (n_0) changes to smaller values and the average number of ion pairs in the cluster (n) changes to smaller values also.

The smaller the average number of ion pairs in the cluster, the lower the peak wave number of this cluster. Thus the peak shift value, which is representative of the difference between the wave number of ion pairs and the wave number of cluster, is smaller for an ionomer with a larger radius metal ion than for an ionomer with a smaller radius metal ion when ion pairs change to clusters as Table I shows.

Although the formation mechanisms are little different between group I ionomers and group II ionomers, the k' values are not the same. We cannot conclude that the peak shift value of group II metal ionomers is smaller than for group I metal ionomers according to Eq. (3). It can be imagined that the number of ion pairs involved in the clusters for group II ionomers is less than for group I ionomers owing to steric hindrance. Consequently, the peak shift value of carboxylate group in the region of 1480–1670 cm^{-1} for group II ionomers is smaller than that for group I ionomers (see Fig. 14 and Table I).

From this discussion, it can be appreciated that the metal ions play an important role in the structures of the ionomers.

II. THE SPECIAL COORDINATION COMPLEX FORMATION MECHANISM

By comparing spectra of all alkali and alkaline earth metal ionomers with those for transition metal (copper, zinc) ionomers (see Figs. 2–14 and Table I), it can be seen that there are differences between them. For these transition metal ionomers with increasing degree of neutralization, the peak intensities at the 1698 cm^{-1} decrease as for the alkali or alkaline earth ionomers, but no peak shift or band broadening appears. Meanwhile, new peaks in the region of 1480–1670 cm^{-1} appear, which are the same phenomena as for alkali or alkaline earth metal ionomers. These quite different characteristics must be

caused by a different formation mechanism that is based on the differences of the atomic structure between the transition metals and group I and group II metals.

It is supposed that the valence bond theory can be applied to the polymer formation mechanism whereby these phenomena can be interpreted.

From the valence bond point of view, the formation of a coordination compound is a reaction between a Lewis base (ligand) and a Lewis acid (metal or metal ion) with the formation of a coordinate covalent bond between the ligand and the metal.²¹

For the zinc ionomer the three 4*p* orbitals and one 4*s* orbital are hybridized. Four equivalent “*sp*³” orbitals are formed that can accept four ligands. The complexes formed are tetrahedral or square planar structures. Thus a symmetrizable single peak of carboxylate groups appear in the FT IR spectra.

Because these four-coordinate complexes are independent and stable structures, they do not change as the degree of neutralization increases. Therefore, no shifts appear in the 1480–1670 cm^{-1} region. Meanwhile, in this structure the zinc cation should not affect the carbonyl groups because the cations are shielded by nonionic macromolecules (polyethylene). Consequently, peak shifts do not appear in the 1698- cm^{-1} region.

For copper (Cu^{2+}) ionomer three kinds of hybridization are possible,²² *dsp*² inner orbitals, *dsp*² outer orbitals, and *sp*³ orbitals. However, whichever kind of hybridization is formed, as the degree of neutralization changes, a new symmetrical and stable single peak in the region of 1480–1670 cm^{-1} should appear because the complexes with square planar or tetrahedral structures are symmetrical and stable structures. Therefore peak shifts are not observed. At the same time, no peak shifts appear in the 1698- cm^{-1} region, the reason is the same as for the zinc ionomer described previously.

It cannot become a six coordination number complex because in this case distorted octahedral structures will appear, and the peak will not be symmetrizable. Further study of the structure of transition metal ionomers is necessary.

III. EVIDENCE FOR THE TWO FORMATION MECHANISMS AND MODELS OF IONOMERS

Water Immersion of Ionomers

Figures 15 and 16 were copied from the thesis of Brozoski. These figures show the results of water

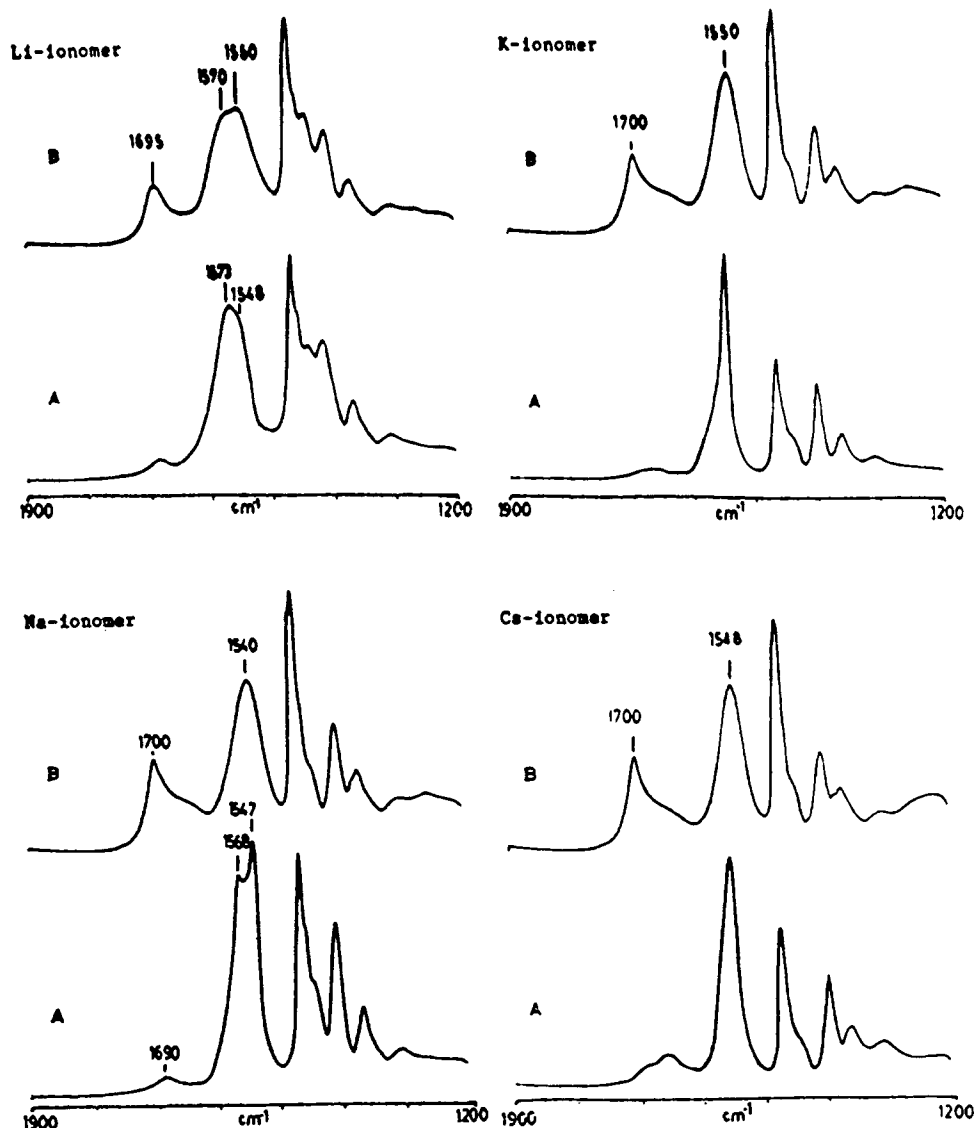


Figure 15 FT IR spectra (in the 1200–1900 cm^{-1} range) of water immersion results of completely ionomers: (A) after quenching in liquid nitrogen from the melt; (B) after water immersion, lithium ionomer 39 days, sodium ionomer 39 days, potassium ionomer 45 days, cesium ionomer 46 days.

immersion of the completely neutralized ionomers, which include alkali metal, alkaline earth, and zinc salts. Spectra A are for samples not immersed in water; spectra B are for samples immersed in water for at least 20 days. Comparing spectra A and B, it can be seen that:

1. After these ionomers were immersed in water for a long time the intensity of the spectra of carbonyl groups at the region of 1698 cm^{-1} is much stronger than before water immersion. No change occurred in the zinc ionomer.
2. The intensity of the cluster peak was less af-

ter water immersion than before water immersion, or it can be said that some of the cluster peaks disappeared. No change appeared in the zinc ionomer spectrum.

From these phenomena it can be further concluded that there are different formation mechanisms for alkali, alkaline earth metal, and transition metal zinc ionomers. At the same time, it also can be shown that there are chemical equilibria between multiplets and clusters during cluster formation whether they are alkali metal or alkaline earth metal ionomers. As already described, the process of

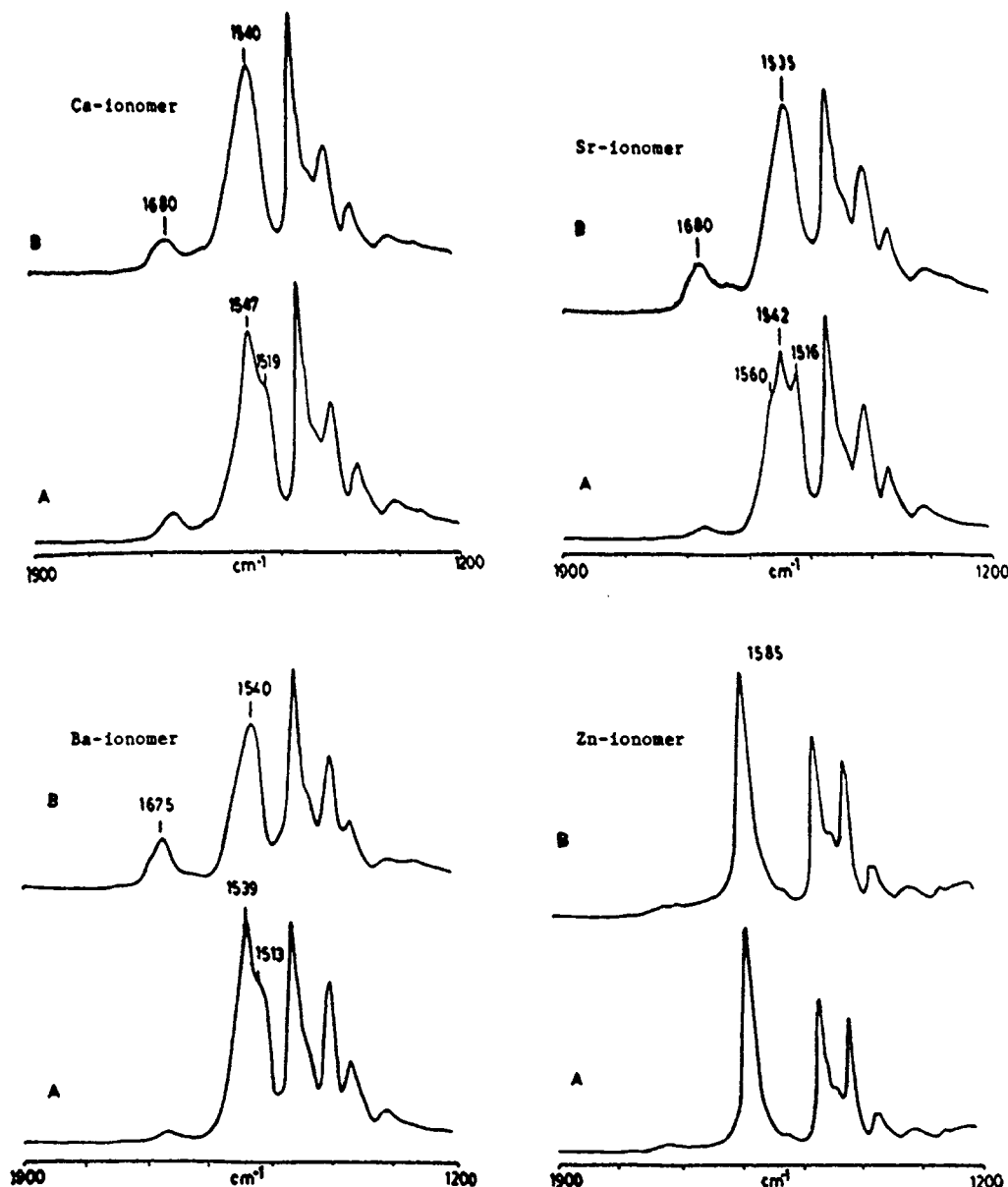


Figure 16 FT IR spectra (in the 1200–1900 cm^{-1} range) of water immersion of completely ionized ionomers: (A) after quenching in liquid nitrogen from the melt; (B) after water immersion, calcium ionomer 24 days, strontium ionomer 21 days, barium ionomer 39 days, zinc ionomer 39 days. Barbara A. Brozoski, Ph.D Thesis, Dept. of Material Science and Engineering, The Pennsylvania State University, 1983, p. 112, 115, 117, 119, 124, 126, 128, 131.49. [Avail. Univ. Microfilms Order No. DA8327566 116 pp.]

cluster formation is a chemical equilibrium process. After ionomers that involved alkali and alkaline earth metal, respectively, were immersed in water for a long time, the chemical equilibria in the ionomers were reversed. The clusters were dissociated into multiplets gradually by the water. In this case these new multiplet structures are different from the original multiplet structures because the chem-

ical environment is different. More water is involved in it. Therefore, the peak wave numbers of the new multiplets are different from those of the original multiplets involved in alkali and alkaline earth metal ionomers. These new multiplets can be considered as complexes that include water. Also the peaks in the 1698- cm^{-1} region become stronger than those of the original sample because of the reverse chem-

ical reaction. For the zinc ionomer the coordinated complexes were not influenced by water immersion, consequently, no peak changes occur.

Dynamic Thermal Equilibrium between Clusters and Multiplets

According to Eisenberg's theory¹ the cluster is not infinitely stable. At some temperature, T_c , the cluster decomposes, and it is at that temperature that the elastic forces and the electrostatic forces just balance. Since it has been suggested that there are multiplet-cluster structures in alkali and alkaline earth metal ionomers, this effect should be reflected in the results obtained at different temperatures.

Figures 17–19, also from Dr. Brozoski's thesis, are the spectra of the various completely ionized al-

kali, alkaline earth, and transitional metal zinc and copper ionomers at room temperature (A) and 70°C (B).

By comparing these spectra it can be seen that the intensity of the multiplet peak at 70°C is stronger than that at room temperature for all alkali and alkaline earth ionomers, but no change appears for the transitional metal zinc and copper ionomers.

The main reason is that, as Eisenberg described,¹ once this multiplet has been formed, it is completely coated with nonionic chain material, so that the multiplets only contain ionic material whereas clusters contain both ionic and nonionic material. Because of the existence of the nonionic material, there is a balance between elastic and electrostatic forces.

When the temperature increases, the electrostatic force is not affected but the elastic force would be

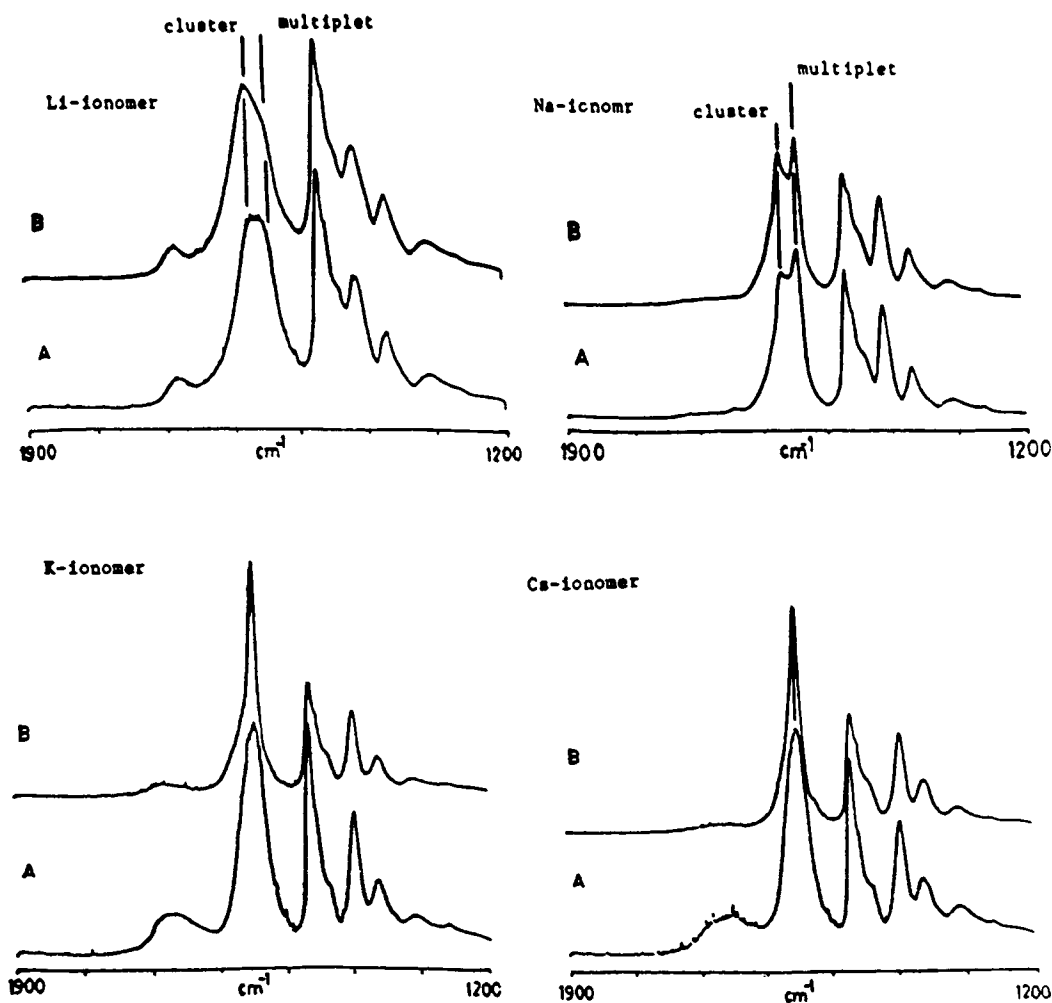


Figure 17 FT IR spectra (in the 1200–1900 cm^{-1} range) of completely ionized lithium, sodium, potassium, and cesium ionomers: (A) at room temperature after quenching in liquid nitrogen, (B) 70°C.

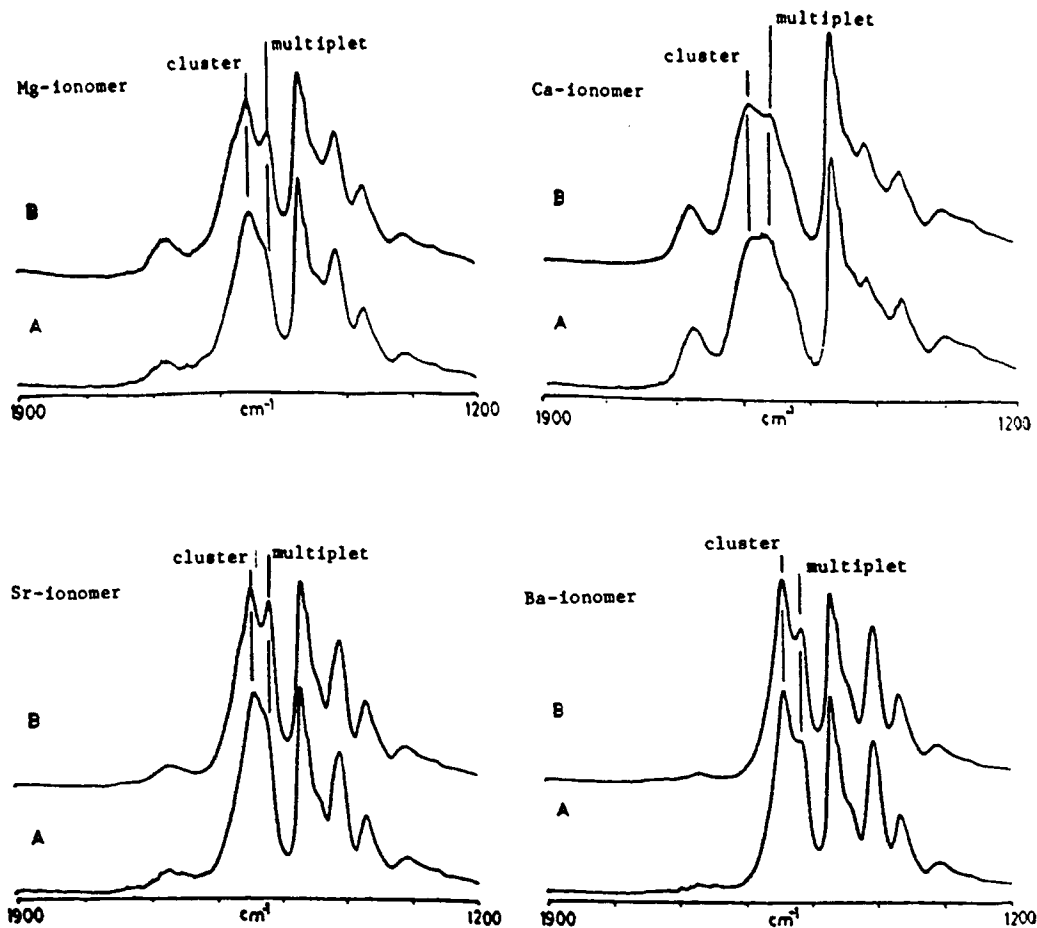


Figure 18 FT IR spectra (in the 1200–1900 cm^{-1} range) of completely ionized magnesium, calcium, strontium, and barium ionomers: (A) at room temperature after quenching in liquid nitrogen, (B) at 70°C.

affected. Therefore, when the balance between the electrostatic force and the elastic force is disturbed some of the original clusters dissociate to multiplets gradually depending on the temperature and the time of heating. This explains the fact that the relative intensities of the multiplet spectra at 70°C are greater than at room temperature.

From the water immersion tests and high-temperature measurements on these ionomers, it can be concluded that there are two quite different formation mechanisms.

SUMMARY AND CONCLUSIONS

Through the investigation and analysis of the peak shifts in the FT IR spectra of different ionomers at different degree of neutralization, it is concluded that:

1. There are two mechanisms and models for ionomers. The multiplet–cluster model is suitable for alkali and alkaline earth metal ionomers. The coordination complex model is suitable for the transition metal ionomers such as copper and zinc ionomers.
2. During ionomer formation there are some differences between alkali and alkaline earth ionomers. The former form clusters directly through several chemical equilibria. The latter form clusters through closing and opening ring processes as well as the chemical equilibria.
3. Through the analysis of shift values it can be deduced that the metal cations effect the ionomer structures strongly.
4. By comparison of these spectra for a metal ionomer at room temperature and 70°C as well as the spectra of a metal ionomer before

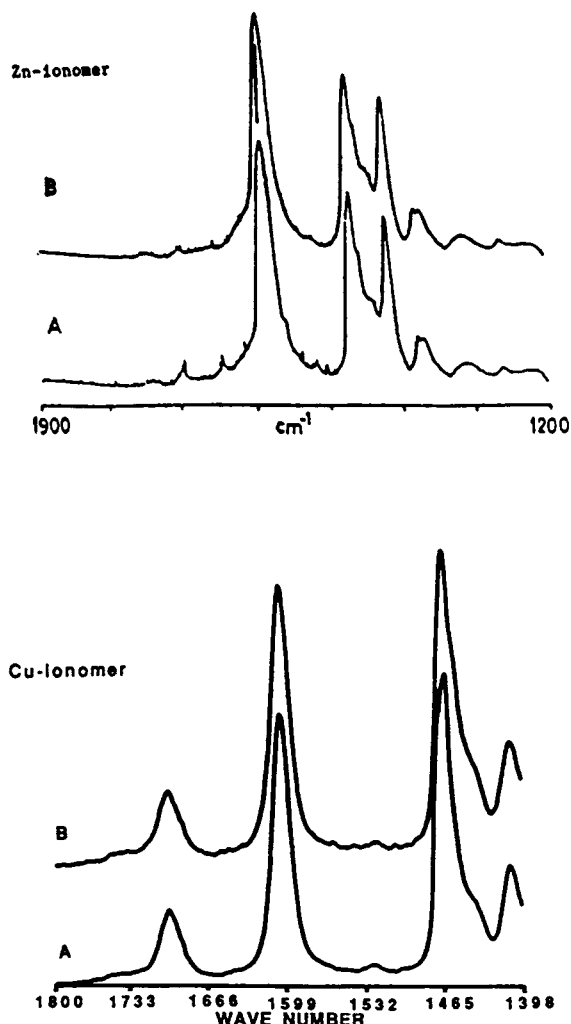


Figure 19 FT IR spectra (in the 1200–1900 cm^{-1} range) of completely neutralized zinc ionomer and 79% neutralized copper ionomer: (A) at room temperature after quenching in liquid nitrogen, (B) at 70°C. Barbara A. Brozowski, Ph.D Thesis, Dept. of Material Science and Engineering, The Pennsylvania State University, 1983, p. 25, 29, 32, 34, 37, 40, 42, 44, 49. [Avail. Univ. Microfilms Order No. DA8327566 116 pp.]

and after water immersion, the existence of two mechanisms and models were indicated.

5. Further studies are required to determine the structure of transition metal ionomers in more detail.

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