Macromolecules 1990, 23, 2339–2345

Acid Salts and the Structure of Ionomers

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ABSTRACT: Carboxylic acid salts, which are compounds involving strong hydrogen bonds between carboxyl and carboxylate groups, have been largely ignored in previous studies of the microstructure of ionomers. In the vast majority of commerical applications of ionomers that are derived from acrylic or methacrylic acid copolymers, however, the carboxylic acid groups are only partially neutralized and there is a stoichiometric excess of carboxylic acid groups to metal cations present. It is under these circumstances that the formation of acid salts becomes particularly significant. In this work we present infrared studies of anhydrous partially and fully neutralized ethylene-*co*-methacrylic acid copolymer samples. Zinc ions were introduced into the sample by immersion in a dilute solution of diethylzinc in hexane, which results in a material that resembles a "skin–core" composite of a fully neutralized tetracoordinated zinc carboxylate skin and an essentially pure acid copolymer core. This is a quasi-equilibrium situation, since mixing of the skin and core is prevented by the restricted mobility of the fully neutralized zinc salt. At elevated temperatures, however, the fully neutralized zinc salt and the pure acid copolymer mix and the transformation to hexacoordinated zinc carboxylates and zinc acid salts is observed in the infrared spectrum. Significantly, incorporation of a flexible miscible polymer, poly(vinyl methyl ether), reduces the temperature at which this transition occurs. The results are discussed in terms of a series of equilibria. Acid salts are local structures that need to be considered when developing models of ionomers.

Introduction

Ionomers are ion-containing polymers, typically with hydrocarbon backbones, that contain a relatively small number of acid groups (e.g., carboxylic, sulfonic, or phosphoric acids, etc.). These acid groups are incorporated into the main chain or are present as pendant groups and may be partially or fully ionized. Research on the microstructure of ionomers has been extensive over the past two decades because of the unique physical properties that these materials possess and their importance as commercial materials. Much study has been devoted to the determination of the size and structure of the ionic domains and the correlation between molecular structure and properties, but there are still many open questions. The reader is referred to a number of excellent books and reviews for detailed discussions of these issues.[1-7]

Several models have been proposed to describe the microstructure of ionomers, one of the first being the multiplet-cluster model proposed by Eisenberg.[8] Multiplets are localized structures describing the arrangement of ionized acid groups around specific cations. Clusters, on the other hand, are defined as groups of several multiplets that form a domain in the material which is locally rich in ionic species but also contains a significant amount of hydrocarbon. Several years ago we reported the results of infrared studies of ethylene-*co*-methacrylic acid (EMAA) copolymer films that had been completely neutralized with various metal cations.[9,10] Emphasis was placed upon the interpretation of the "fine structure" present in the carboxylate asymmetric stretching region of the infrared spectra of various metallic salts of an EMAA copolymer. From a consideration of the known coordination tendencies of the different cations, together with a symmetry analysis of the most probable structures, we were able to show that the experimental infrared results were entirely consistent with the presence of specific local structures (multiplets).[11]

There are a number of factors that frustrate molecular spectroscopists and make the characterization of ionomers difficult. First, ionomers are hydrophilic and normally contain polar sites that are vulnerable to hydrogen bonding by proton donors or acceptors. Thus it is not surprising that the presence of water can detrimentally effect the physical, mechanical, and electrical properties of ionomeric materials. From an infrared spectroscopist's point of view, water tends to complicate the spectra of ionomers by broadening the normal vibrations of interest.[10] In addition, in the presence of water, salt structures established in fully neutralized ionomers can transform into other species, such as acid salts and carboxylic acid dimers, depending upon the particular cation studied.[12] Accordingly, we believe that the meticulous elimination of water is a necessary prerequisite for initial experiments if we are to correctly interpret the infrared spectra of ionomers.

Second, although the infrared spectra of anhydrous fully neutralized ionomeric materials are easier to intrepret, in commercial applications EMAA ionomers are compounded so as to be only partially neutralized.[13] This is principally due to the extraordinary high melt viscosities of fully neutralized materials, which makes them intractable and precludes fabrication in contemporary processing equipment. Partial neutralization unavoidably increases the number and nature of the local structures present, but if studied initially in the absence of water, this should not pose an unmanageable problem and merely represents the next level of complexity.

Finally, introducing metal cations into the EMAA copolymer without at the same time adding water or some unwanted chemical species to the sample is not a trivial exercise. Attempts to infuse ions into previously prepared EMAA films using metal complexes that are soluble in organic solvents but at the same time do not dissolve the EMAA copolymer, such as acetyl acetonates, were not very successful. Ligand residues are invariably trapped in the films and complicate the interpretation of the infrared spectra. In the past, fully neutralized ionomer films were prepared for infrared analysis by pressing at 190 °C the dried precipitate formed during the refluxing of an EMAA copolymer with a stoichiometric

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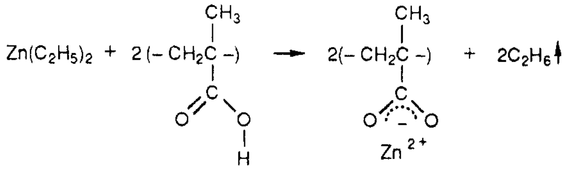
excess of the relevant metal hydroxide in THF/water mixtures.[9,10] This technique can only be applied to the preparation of fully neutralized ionomers, since in the partially neutralized counterparts there inevitably exist residual un-ionized acid groups that chemically transform to anhydrides at the temperatures required to press thin films.[14]

The above three paragraphs describe an obvious predicament. Partially neutralized EMAA copolymers, where only a very modest temperature range exists between the glass transition temperature (T_g) and the onset of chemical modification (anhydride formation), where the materials are hydrophilic and water is known to degrade the resolution of infrared spectra and, more importantly, play a role in determining the type and distribution of the local species present, and where the introduction of cations into the material often results in the incorporation of unwanted "additives" and the production of an insoluble, intractable material with a higher T_g, are, to state the obvious, formidable materials to characterize. While we pondered this dilemma it occurred to us that there are two different ideas that might help to resolve these problems. First, our recently reported studies of EMAA blends with polyethers[14,15] demonstrate that the EMAA–poly(vinyl methyl ether) (PVME) system is miscible and that the T_g is significantly depressed in these mixtures. We concluded that the introduction of PVME might enhance mobility of the partially neutralized ionomers, thus eliminating the necessity for studies at temperatures in excess of 140 °C, albeit at the expense of added complexity. Second, the use of metal alkyls, such as diethylzinc ($ZnEt_2$), as the cation source was inspired by the recognition that these compounds can only be used under strictly anhydrous conditions ($ZnEt_2$, for example, is commonly employed in gloveboxes to detect trace amounts of moisture) and that upon reaction with the EMAA copolymer the byproduct of neutralization is ethane gas, which escapes and thus does not complicate the infrared spectrum.



$$Zn(C_2H_5)_2 + 2(-CH_2C(CH_3)(COOH)-) \longrightarrow 2(-CH_2C(CH_3)(COO^-)-)\,Zn^{2+} + 2C_2H_6\uparrow$$

In this paper, we initially discuss both the fully and partially neutralized anhydrous zinc ionomers of an EMAA copolymer containing 26 wt % methacrylic acid (EMAA[26]) using $ZnEt_2$ as the source of Zn^{2+} cations. We will then turn our attention to a discussion of the results of a similar study, but this time using a blend of EMAA[26] with PVME. Finally, the ramifications of these results will be considered in terms of the local structures present in partially neutralized ionomers derived from EMAA copolymers and the like.

Experimental Section

The ethylene–methacrylic acid (EMAA) copolymer used in this study was synthesized in the laboratories of the E. I. du Pont de Nemours & Co. The EMAA copolymer contains 26 wt % methacrylic acid (MAA) and is denoted EMAA[26], following the nomenclature we employed previously.[14] This corresponds to 10.3 mol % MAA on a molar basis. Assuming a random distribution of MAA units in the copolymer, this yields an average number of 19 methylene groups per MAA unit. Results obtained from differential scanning calorimetry (DSC) indicate that the EMAA[26] copolymer crystallizes to a very limited extent. Multiple peaks were observed in the DSC thermogram, and a crystalline melting point (T_m) of about 50 °C was determined at the peak maximum of the highest temperature transition. The glass transition temperature (T_g) of this EMAA[26] copolymer is in the range of 25–32 °C. Poly(vinyl methyl ether) (PVME) was purchased from Polysciences Inc. It is an amorphous polymer with a T_g of −27 °C.

Thin films of the EMAA[26] copolymer were prepared for infrared and thermal analysis by casting from 1% THF solution (w/v) onto KBr windows and glass slides, respectively. After a majority of the solvent had evaporated, the films were transferred to a vacuum desiccator to remove residual solvent and were then stored under vacuum over fresh phosphorus pentoxide (P_2O_5) to minimize moisture adsorption. A similar procedure was employed to prepare thin films of the EMAA[26] copolymer blend with PVME (50/50 by weight). A 1.0 M diethylzinc ($ZnEt_2$) solution in hexane was purchased from Aldrich Chemical Co. The $ZnEt_2$ solution was diluted further with 2-fold anhydrous hexane in a helium-purged dry glovebox. The EMAA[26] copolymer (or blend) films, supported on their KBr windows or glass slides, were then transferred to the glovebox and introduced into the dilute $ZnEt_2$ solution. After exposure to the $ZnEt_2$ solution for different lengths of times (to give varying degrees of overall neutralization), the films were removed and placed in small vacuum desiccator over P_2O_5 and evacuated for at least 24 h.

Infrared spectra were recorded on a Digilab FTS-60 FT-IR spectrometer at a resolution of 2 cm^{-1} except otherwise noted. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller. This device has a reported accuracy of ±0.1 °C. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.

Results and Discussion

Details of the temperature dependence of the infrared spectra of EMAA copolymers have been presented in a previous paper,[14] and here we will only give a brief summary. In pure EMMA[26] copolymer at ambient temperature the carboxylic acid groups exist predominantly as dimers (shown schematically in Figure 1B) and have a characteristic infrared carbonyl stretching vibration located at 1700 cm^{-1}. The carbonyl stretching vibration of the monomeric carboxylic acid group, which becomes more apparent with increasing temperature, occurs at 1750 cm^{-1}. At temperatures above about 140 °C, bands attributed to the formation of cyclic and linear anhydrides are observed at 1802/1764 and 1780/1735 cm^{-1}, respectively.[14] In addition, during the synthesis of the EMAA[26] copolymer a minor fraction of the carboxylic acid groups are converted to esters by transesterification and this group is characterized by a relatively weak absorbance at 1735 cm^{-1}. This latter band appears, at best, to be an unfortunate complication, but we will turn this around and use it to our advantage.

Figure 2 shows infrared spectra recorded at room temperature in the range of 1500–1800 cm^{-1} of samples of pure EMAA[26] (denoted A) and the partially (B–D) and fully (E) neutralized EMAA[26]–zinc ionomer films prepared using $ZnEt_2$ in the manner described in the Experimental Section. For explanatory purposes, the spectra are displayed *scale-expanded* to the absorbance of the ester carbonyl band (1735 cm^{-1}), which we can conveniently use as an internal standard. As expected, the pure EMAA[26] spectrum shows only the infrared bands attributed to the carboxylic acid dimer (1700 cm^{-1}) and the ester impurity (1735 cm^{-1}), and there are no other significant absorbances in the 1500–1700-cm^{-1} region of the spectrum. At the other extreme, the spectrum of the fully neutralized ionomer (Figure 2E) also reveals the ester band, but the dominant band is at 1585 cm^{-1}. Varying

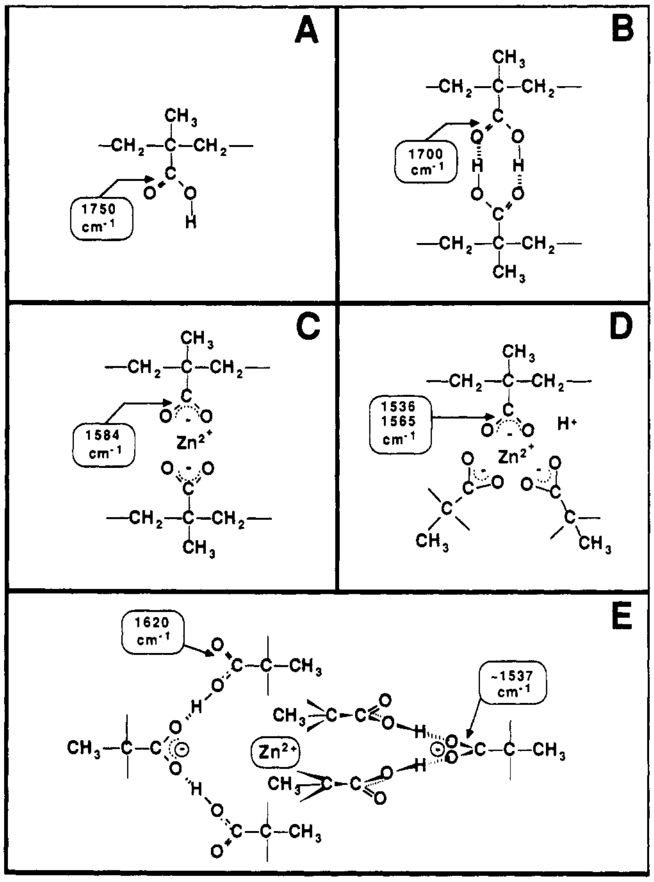


Figure 1. Schematic representation of local structures: (A) carboxylic acid "monomer"; (B) carboxylic acid dimer; (C) tetracoordinated zinc carboxylate; (D) hexacoordinated zinc carboxylate; (E) zinc acid salt.

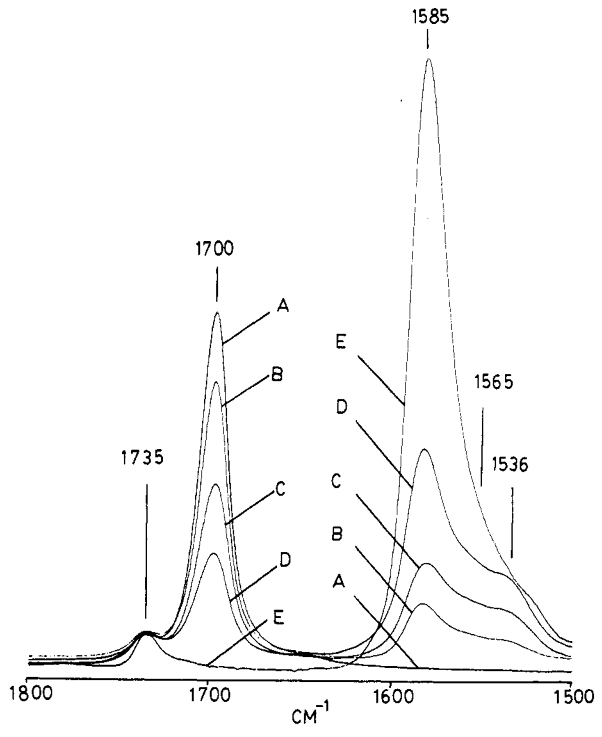


Figure 2. Scale-expanded infrared spectra recorded at room temperature in the range 1850–1500 cm^{-1} of EMAA[26] copolymer films with varying degrees of overall neutralization with zinc ions: (A) pure EMAA[26]; (B) 13%, (C) 40%, (D) 66%, and (E) 100% neutralized (see Table I).

degrees of partial neutralization in the ionomer films, corresponding to the spectra labeled B–D, are evident as the bands attributed to both the carboxylic acid dimer (1700 cm^{-1}) and the carboxylate band (1585 cm^{-1}) are present, but in different intensity ratios. In addition, there are two further bands at 1536 and 1565 cm^{-1}, which appear as a shoulder on the 1585-cm^{-1} band and which are accentuated by second derivative spectroscopy (Figure 3B).

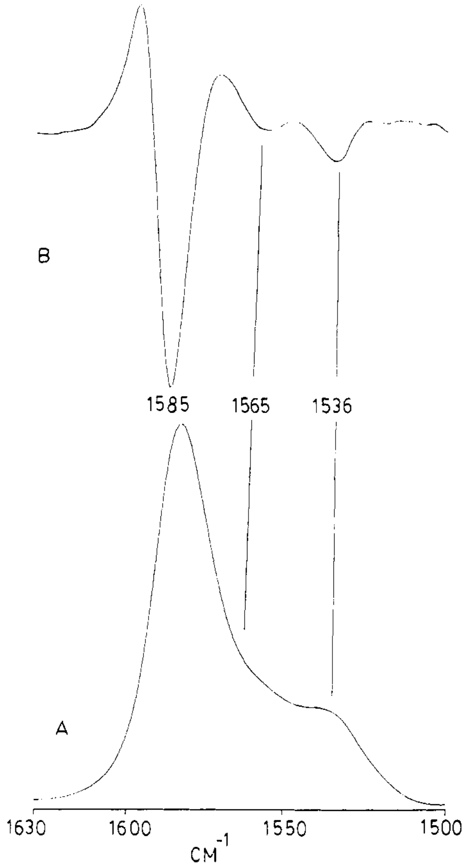


Figure 3. Second derivative spectrum in the range 1500–1630 cm^{-1} of the partially neutralized sample shown in Figure 2D.

From a previously reported symmetry analysis we have assigned the singlet at 1585 cm^{-1} to the asymmetric carboxylate stretching vibration of the tetrahedral structure of the tetracoordinated zinc carboxylate multiplet[11] (shown schematically in a 2-dimensional representation in Figure 1C). The pair of bands at 1536/1565 cm^{-1}, which will become more important and definitive in the forthcoming discussion, are assigned to the hexacoordinated zinc carboxylate multiplet, also shown schematically in Figure 1D. From a consideration of the size of the respective ionic radii, zinc carboxylates are predicted to favor coordination numbers of 4 or 6 and our previous symmetry analysis predicts two infrared active asymmetric carboxylate bands associated with the octahedral structure of a hexacoordinated zinc carboxylate.[11]

Obtaining a quantitative estimate of the degree of neutralization in partially neutralized ionomers is not a trivial problem. As we will see later, in addition to the 1585-, 1565-, and 1536-cm^{-1} bands attributed to zinc carboxylates, there are other infrared absorbances associated with acid salts that have significant absorbances in the 1500–1700-cm^{-1} region of the spectra of the partially neutralized zinc ionomers. Accordingly, the zinc ions are distributed over a number of different structural entities for which we do not have well-established absorption coefficients. Thus any infrared analytical method used to determine the degree of neutralization based on a calibration curve derived from a series of EMAA samples of

Table I
Determination of % Neutralization for EMMA[26]-Zn Ionomers

	ester C=O			acid dimer C=O			
sample	ν, cm^{-1}	$w_{1/2}$, cm^{-1}	A_E[a]	ν, cm^{-1}	$w_{1/2}$, cm^{-1}	A_D[a]	% neutralization
A	1737	15	0.49	1699	18	9.3	0
B	1736	15	1.71	1699	18	28.2	13
C	1735	15	0.44	1698	21	5.0	40
D	1735	15	0.75	1699	22	4.9	66
E	1734	15	0.61				100

[a] Arbitary units.

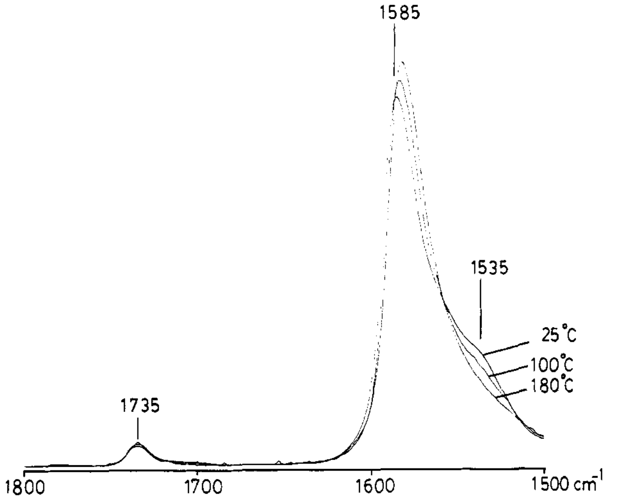


Figure 4. Infrared spectra in the range 1800–1500 cm^{-1} recorded at 25, 100, and 180 °C of a completely neutralized zinc ionomer.

known zinc content using intensity measurements of a single carboxylate band (or the total absorbance of a collection of bands in the 1500–1700-cm^{-1} region) is subject to large errors. An alternative method is to simply measure the ratio of the absorbance of the carboxylic acid dimer to an internal standard such as the 1735-cm^{-1} ester carbonyl band A_D/A_E. From the spectrum of the pure EMAA[26] film sample, we can determine the corresponding absorbance ratio for the completely un-ionized case, $A_D{}^0/A_E{}^0$, and the degree of neutralization is given by

$$\%\ \text{neutralization} = \left[1 - \left\{\frac{A_D}{A_E}\frac{A_E{}^0}{A_D{}^0}\right\}\right] \times 100$$

Note that the absorption coefficients conveniently cancel out in this equation. The degree of neutralization for each of the samples depicted in Figure 2 was determined, and the results are summarized in Table I.

Temperature Studies. Figure 4 shows the effect of temperature on the infrared spectrum of the completely neutralized sample. In brief, little significant change is observed in the spectra at temperatures up to 180 °C, except that the bands at 1536/1565 cm^{-1}, assigned to the hexacoordinated zinc carboxylate multiplet,[9,10] decrease in intensity. The original intensity of these bands is not recovered upon cooling back to room temperature. This we interpret as a transformation of a minor amount of the hexacoordinated into the tetracoordinated zinc carboxylate.

Contrast this behavior with that observed in the spectra recorded as a function of temperature (up to 140 °C and below the onset of anhydride formation) for one of the partially neutralized zinc ionomers. This is shown in Figure 5. Spectra are labeled A–F and represent those

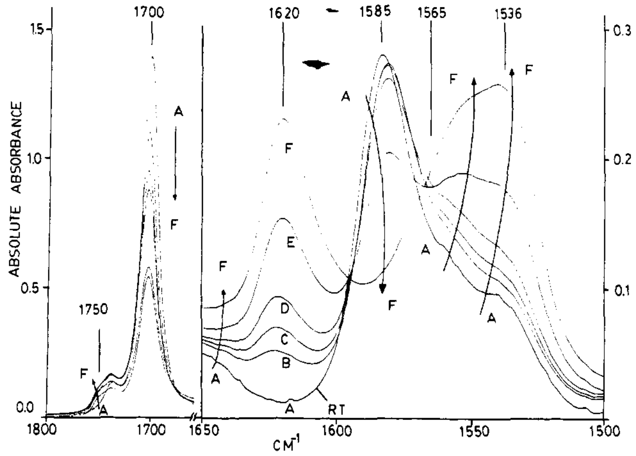
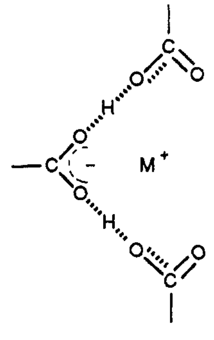


Figure 5. Infrared spectra shown on two different *absolute* absorbance scales in the ranges of 1800–1650 and 1650–1500 cm^{-1} of a partially neutralized zinc ionomer recorded as a function of increasing temperature: (A) room temperature; (B) 100, (C) 110, (D) 120, (E) 130, and (F) 135 °C.

recorded on an *absolute absorbance scale* at room temperature, 100, 110, 120, 130, and 135 °C. The carboxylic acid carbonyl (1800–1650 cm^{-1}) and carboxylate (1650–1500 cm^{-1}) stretching regions of the infrared spectra are shown separately for expository convenience. Between room temperature and 100 °C there are no substantial changes observed in the spectra. Above 100 °C, however, major infrared spectral changes are observed. First, the bands attributed to hexacoordinated zinc carboxylates (1536/1565 cm^{-1}) increase in intensity, while the band at 1585 cm^{-1}, associated with tetracoordinated zinc carboxylates, decreases. Second, there is a large decrease in the relative intensity of the carboxylic acid dimer band (1700 cm^{-1}) and a small, but significant, increase in the relative intensity of the monomeric carboxylic acid band at 1750 cm^{-1}, also with increasing temperature. The most conspicuous change, however, is the appearance and growth of a new absorption band at 1620 cm^{-1}. This band can be assigned to an acid salt structure,[16,17] which is depicted schematically below and, for specifically the zinc acid salt, in Figure 1E.



acid salt structure

Acid salts have very short hydrogen bonds, and as the strength of the hydrogen bond increases the hydrogen atom is not so clearly identified as more strongly associated with one atom or the other.[16,17] This causes a very large shift in frequency of about 130 cm^{-1} for the carbonyl band of the carboxylic acid group from 1750 to 1620 cm^{-1}. A second overlapping band associated with acid salts also exists in the 1500–1650-cm^{-1} region of the spectrum due to the hydrogen-bonded carboxylate group and appears at approximately 1537 cm^{-1}, overlapping the doublet due to the hexacoordinated carboxylate near 1565/1536 cm^{-1}.

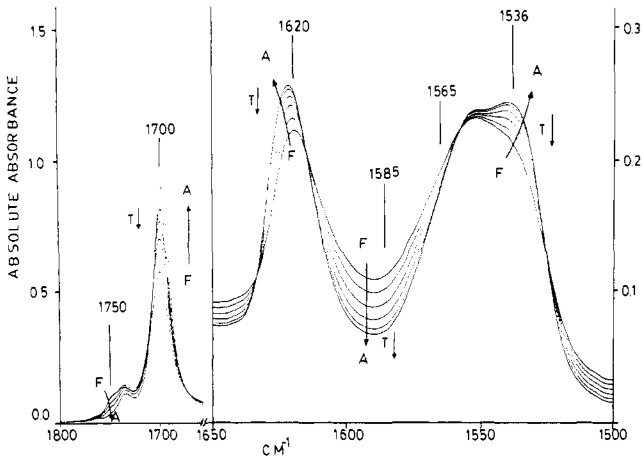


Figure 6. Infrared spectra of the same sample employed in Figure 5 recorded as a function of decreasing temperature from 135 °C: (A) room temperature; (B) 100, (C) 110, (D) 120, (E) 130, and (F) 135 °C.

Now let us consider what happens to the infrared spectrum when we cool the *same* sample back to room temperature. This is illustrated in Figure 6. Spectra recorded as a function of decreasing temperature on the *same absolute absorbance scale* are labeled A–F and correspond to the same temperatures as in the heating cycle (Figure 5). The most striking features are the conspicuous absence of the 1585-cm^{-1} band (the tetracoordinated zinc carboxylate) and the prominent presence of the 1536/1565-cm^{-1} doublet (the hexacoordinated zinc carboxylate) and the 1620- and 1537-cm^{-1} bands (zinc acid salt). (Naturally, the 1537-cm^{-1} band of the acid salt is superimposed upon the 1536-cm^{-1} band of the hexacoordinated zinc carboxylate, and in these spectra its presence can only be inferred by the anomalous intensity behavior of the observable doublet. In other spectra, however, especially those recorded from samples containing a large excess of unionized acid groups, it can be clearly observed.) Of equal importance is the behavior of the band attributed to the hydrogen-bonded carboxylic acid dimer (1700 cm^{-1}). As expected from equilibrium considerations, the intensity of this band increases with decreasing temperature while, concurrently, the relatively weak band associated with the carboxylic acid monomer (1750 cm^{-1}) decreases. But, it is the comparison of the room-temperature spectra before (Figure 5A) and after (Figure 6A) the temperature cycle that is germane. There is an obvious decrease in the absolute absorbance of the 1700-cm^{-1} band, revealing a decrease in the concentration of carboxylic acid groups.

Before we attempt to interpret these results let us also consider the results of one further experiment. A partially neutralized EMAA[26]–Zn ionomer sample, prepared as described previously using $ZnEt_2$ and of comparable degree of neutralization to that employed above (Figure 5), was heated rapidly in the FTIR spectrometer to 110 °C (close to the temperature where changes were initially observed). Spectra were recorded at 110 °C as a function of time over a period of 20 h and are shown in Figure 7. In essence, there is a ponderously slow, but inexorable, increase in the absorbance of the 1620-, 1565-, and 1536-cm^{-1} bands at the expense of the absorbance of the bands at 1700 and 1585 cm^{-1}. Incidentally, performing the same experiment at higher temperatures (up to 140 °C, the onset of anhydride formation) increases the rate of the conversion but does not affect the outcome.

Interpretation of the Results. The results described in the above three paragraphs strongly imply a transformation from a nonequilibrium mixture or "sandwich" of essentially tetracoordinated zinc carboxylate salts and carboxylic acid groups (present predominantly as dimers) in the *original* partially neutralized EMAA[26]–Zn ionomer film to an equilibrium mixture of hexacoordinated zinc carboxylates, zinc acid salts, and residual carboxylic acid groups (mainly dimers).

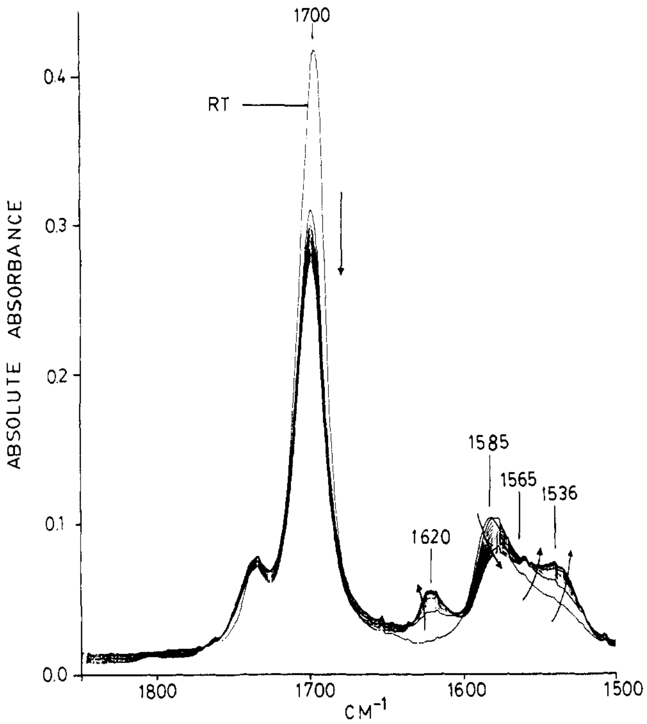


Figure 7. Infrared spectra in the range of 1800–1500 cm^{-1} of a partially neutralized zinc ionomer recorded at 110 °C as function of time.

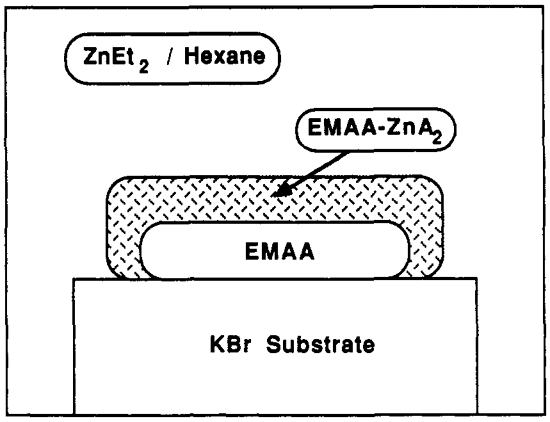


Figure 8. Schematic diagram of the "skin–core" composite formed upon immersing the EMAA[26] copolymer into the $ZnEt_2$/hexane solution.

It should be emphasized that we did not set out to prepare nonequilibrium, partially neutralized, ionomers using the $ZnEt_2$ method described in the Experimental Section. Our principal objectives were to eliminate water and extraneous ligands in the preparation of partially neutralized ionomer films suitable for infrared analysis. Thus, the initial formation of the ionomeric sandwich material described above was purely serendipitous. Nonetheless, having produced such a material, it was easy to conceive of a "skin" being formed as the $ZnEt_2$ diffuses into the EMAA copolymer. This is depicted schematically in Figure 8. The almost instantaneous reaction between $ZnEt_2$ and the carboxylic acid proton dictates that carboxylates are formed at the interface between

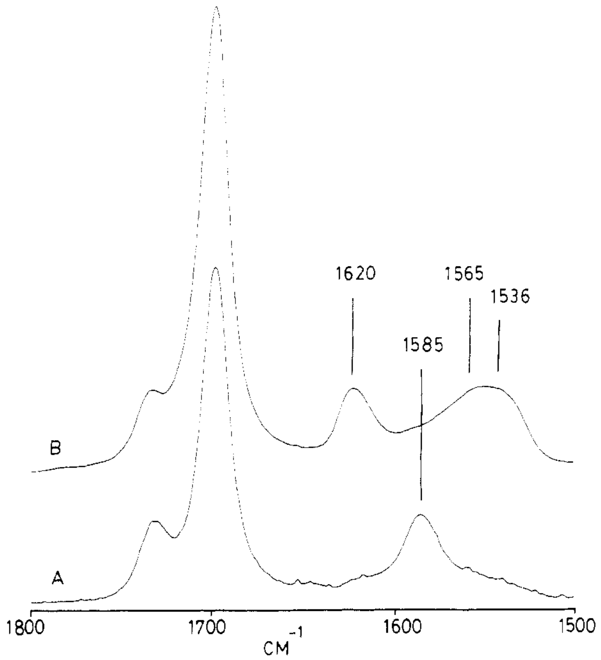


Figure 9. Infrared spectra in the range of 1800–1500 cm^{-1}: (A) "sandwich" of a completely neutralized zinc ionomer film and pure EMAA[26] recorded at room temperature; (B) same sample recorded at room temperature after annealing overnight at 110 °C.

the skin and core of the material. The skin thus formed has a high concentration of zinc and is essentially the same as that of the totally neutralized sample. Conversely, the core is practically pure EMAA copolymer. Furthermore, as the skin is fully neutralized, its T_g is elevated and there is insufficient mobility for the skin to mix with the core, leading to a nonequilibrium situation. In infrared terms, the spectrum of such a material should therefore resemble the coaddition of the spectra of the fully neutralized zinc ionomer (Figure 4) and the pure EMAA[26] copolymer (Figure 1A), which it does. When the temperature of the sample is increased, a point is reached where there is presumably sufficient mobility to permit the skin and core to mix. Now there is a stoichiometric excess of carboxylic acid groups, and the transformation to hexacoordinated zinc carboxylates and zinc acid salts occurs.

Corroborating evidence for the skin–core model was obtained from an additional simple experiment. A fully neutralized EMAA[26]–Zn ionomer film was prepared by the $ZnEt_2$ method (the infrared spectrum being identical with that shown in Figure 4). A second film of pure EMAA[26] was then deposited on top of the fully neutralized EMAA[26]–Zn ionomer film from a solution in THF. After evaporation of the THF overnight in a vacuum desiccator over fresh P_2O_5, the infrared spectrum shown in Figure 9A was recorded. The spectrum of this bilayer film closely resembles that of the original partially neutralized EMAA[26]–Zn ionomer film (Figure 5A). After annealing at 110 °C overnight, the infrared spectrum shown in Figure 9B was recorded. It is rewarding to see that the infrared band attributed to tetracoordinated zinc carboxylate salts disappears in favor of hexacoordinated zinc carboxylates and zinc acid salts in precisely the same manner as the original partially neutralized EMAA[26]–Zn ionomer film.

Equilibrium Considerations. A description of the chemistry occurring in partially neutralized zinc ionomers may be represented by a series of simple equilibria as depicted in Scheme I.

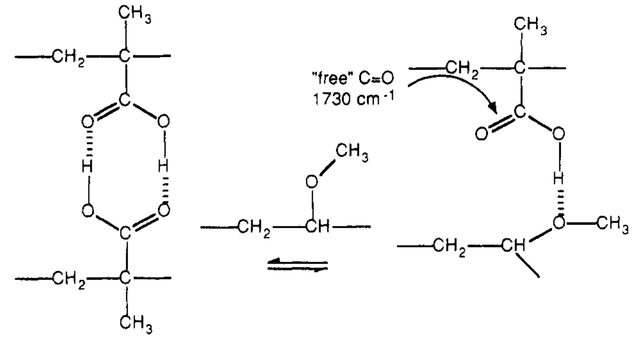


Figure 10. Schematic diagram depicting the carboxylic acid–ether interaction.

There are some important implications of the equilibrium scheme presented in Scheme I. First, in the presence of a stoichiometric equivalent or an excess of zinc cations,

Scheme I

$$2AH \overset{K_1}{\rightleftharpoons} [AH\cdots AH] \quad \text{acid dimer}$$

$$ZnEt_2 + 2AH \xrightarrow{K_2} ZnA_2 + 2EtH\uparrow \quad \text{tetracoordinated zinc carboxylate}$$

$$ZnA_2 + AH \overset{K_3}{\rightleftharpoons} [ZnA_3]^-H^+ \quad \text{hexacoordinated zinc carboxylate}$$

$$ZnA_2 + 4AH \overset{K_4}{\rightleftharpoons} [(AH)_2\cdots AZnA\cdots (HA)_2] \quad \text{zinc acid salt}$$

the tetracoordinated zinc salt will be formed. It is only when there is a stoichiometric excess of carboxylic acid groups that zinc acid salts and the hexacoordinated zinc salt are formed. Given that partial neutralization is the rule in commercial applications of EMAA ionomers, materials prepared using zinc cations can be expected to contain a distribution of species that depend upon the degree of neutralization and include carboxylic acids (predominantly dimers), tetra- and hexacoordinated zinc salts, and zinc acid salts.

EMAA[26]–PVME Blend Neutralized with $ZnEt_2$. We have inferred that the skin formed when $ZnEt_2$ reacts with the EMAA[26] copolymer is intrinsically identified with the interactable fully neutralized Zn ionomer. Only at temperatures exceeding about 110 °C does there appear to be enough mobility to facilitate mixing with nearby EMAA[26] carboxylic acid groups. As mentioned in the introduction, we surmised that blending EMAA[26] with an amorphous *miscible* polymer having a low T_g, such as PVME (T_g = −27 °C), might serve to "plasticize" the subsequently formed ionomer, thus enhancing mobility of the overall system. If true, this should result in a lowering of the temperature of the transformation of the tetracoordinated zinc salts into hexacoordinated zinc salts and zinc acid salts. In miscible blends EMAA–polyether blends,[14] the ether oxygen competes with the self-association (dimer formation) of carboxylic acid groups to establish a hydrogen bond in a manner schematically depicted in Figure 10. Spectroscopically, we observe this interaction in the infrared spectrum as a band attributed to a "free" carbonyl group at 1730 cm^{-1}. A secondary point of interest, therefore, pertains to fate of the favorable intermolecular interactions that exist in a miscible blend of EMAA[26] and PVME upon the introduction of zinc ions.

Scheme II

$$2\mathrm{AH} \overset{K_1}{\rightleftharpoons} [\mathrm{AH\cdots AH}] \qquad \text{acid dimer}$$

$$\mathrm{AH} + \mathrm{E} \overset{K_1'}{\rightleftharpoons} [\mathrm{AH\cdots E}] \qquad \text{acid–ether “complex”}$$

$$\left.\begin{aligned} &\mathrm{ZnEt_2} + 2\mathrm{AH} \xrightarrow{K_2} \mathrm{ZnA_2} + 2\mathrm{EtH}\uparrow \\ &\mathrm{ZnEt_2} + 2[\mathrm{AH\cdots E}] \xrightarrow{K_2'} \mathrm{ZnA_2} + 2\mathrm{EtH}\uparrow + 2\mathrm{E} \end{aligned}\right\} \text{tetracoordinated zinc carboxylate}$$

$$\left.\begin{aligned} &\mathrm{ZnA_2} + \mathrm{AH} \overset{K_3}{\rightleftharpoons} [\mathrm{ZnA_3}]^{-}\mathrm{H}^{+} \\ &\mathrm{ZnA_2} + [\mathrm{AH\cdots E}] \overset{K_3'}{\rightleftharpoons} [\mathrm{ZnA_3}]^{-}\mathrm{H}^{+} + \mathrm{E} \end{aligned}\right\} \text{hexacoordinated zinc carboxylate}$$

$$\left.\begin{aligned} &\mathrm{ZnA_2} + 4\mathrm{AH} \overset{K_4}{\rightleftharpoons} [(\mathrm{AH})_2\cdots\mathrm{AZnA}\cdots(\mathrm{HA})_2] \\ &\mathrm{ZnA_2} + 4[\mathrm{AH\cdots E}] \overset{K_4'}{\rightleftharpoons} [(\mathrm{AH})_2\cdots\mathrm{AZnA}\cdots(\mathrm{HA})_2] + 4\mathrm{E} \end{aligned}\right\} \text{zinc acid salt}$$

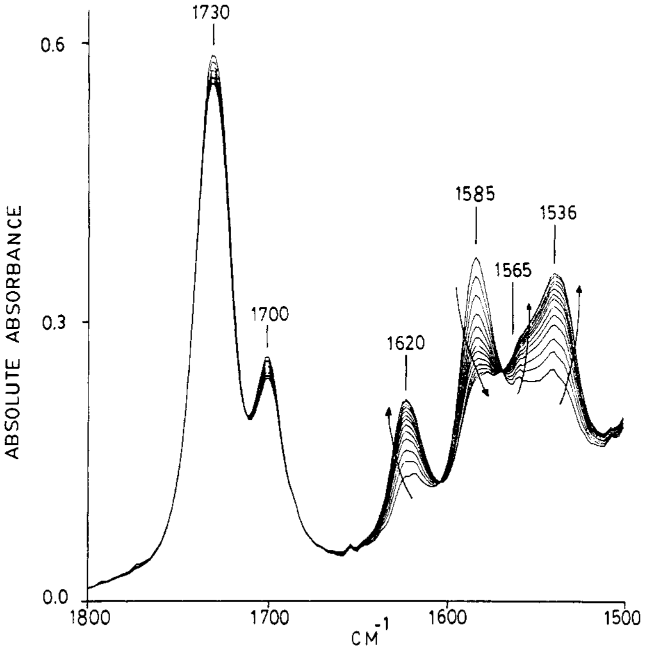


Figure 11. Infrared spectra in the range of 1800–1500 cm^{-1} of a partially neutralized zinc ionomer derived from a 50/50 wt % blend of EMAA[26] and PVME recorded at 80 °C as a function of time.

Films of a 50/50 wt % blend of EMAA[26] and PVME were cast from THF solution onto a KBr window and thoroughly dried over P_2O_5 in a vacuum desiccator. As in the previous experiments involving the pure EMAA copolymer, the blend films were handled in a drybox and immersed in $ZnEt_2$/hexane solution for the time necessary to prepare a film in which only a fraction of the carboxylic acid groups are neutralized. In a series of separate infrared temperature experiments it was determined that the onset of the transformation of the tetracoordinated zinc salts into hexacoordinated zinc salts and zinc acid salts occurs between 70 and 80 °C. This is some 30 °C lower in temperature than that observed for the film of pure EMAA[26] and appears to substantiate the "plasticization" hypothesis mentioned above. Figure 11 shows a typical example of this transformation as a function of time (over a period of 6 h) at the constant temperature of 80 °C. Here we see the familiar increase of the bands attributed to hexacoordinated zinc carboxylate salts and zinc acid salts at the expense of the bands associated with tetracoordinated zinc carboxylates. Smaller changes are also observed in the band intensities of those attributed to acid dimers and acid–ether interactions (the free C=O band at 1730 cm^{-1}). As before, we can represent the chemistry occurring in partially neutralized zinc ionomer blends by a series of simple equilibria as depicted in Scheme II.

Ramifications of This Work. We have seen that in the case of the fully neutralized zinc ionomer of EMAA copolymers a tetracoordinated zinc salt is formed. Since zinc is divalent and the tetracoordinated zinc salt has a coordination number of 4, this results in a local structure that is hydrolytically stable with a balanced charge. As we have demonstrated before, immersing the fully neutralized zinc ionomer film in water does not affect the infrared spectrum and there is no evidence for the transformation of this zinc salt into any other entities.[12] However, in the presence of a stoichiometric excess of carboxylic acid groups (the partially neutralized case), tetra- and hexaccordinated zinc salts, zinc acid salts, and carboxylic acid dimers will all exist in concentrations dependent upon the relevant equilibrium constants.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation, Polymers Program, the Shell Foundation, E. I. du Pont de Nemours & Co., and ARCO Chemical Co.

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