derivatives.

Conclusions

The mechanical relaxation behavior of the 1.25 mequiv/g IEC derivatives is readily interpretable on the basis of the "standard ionomer model". That is, the salt groups aggregate to form a separate microphase that has observable mechanical properties of its own. The fluorocarbon matrix contains considerable quantities of non-phase-separated polar groups and these modify its properties so that it no longer behaves exactly like poly(tetrafluoroethylene). The ester and acid derivatives appear to be one-phase materials in the dry state but it is likely that the acid groups cluster to form a separate polar phase in the presence of water.

The 1.80 mequiv/g IEC derivatives contain such a large quantity of polar groups (36 mol %) that they appear to be primarily one-phase materials regardless of whether they are in the ester, acid, or salt form. Any less polar fluorocarbon phase must be present as a minor component and it must contain very significant quantities of polar groups so that its properties are not very different from those of the polar or "ionic" phase.

The morphology of these derivatives needs to be investigated in detail and small-angle X-ray scattering studies are currently under way.

In general, the perfluorocarboxylate derivatives studied here absorb much less water and show much slower rates of neutralization than comparable perfluorosulfonate derivatives examined previously.

The tetrabutylammonium derivatives, although true salts, exhibits flow at experimentally accessible temperatures and are thus processible. They also dissolve in polar solvents such as dimethylformamide and water.

Acknowledgment. We are grateful to Drs. Ukihashi and Miyake of the Asahi Glass Co. for providing perfluorocarboxylate starting materials. We are also grateful to the Mitsubishi Petrochemical Co. for providing support for one of us (Y.N.). Acknowledgment is made to the Materials Research Laboratory of the University of Massachusetts for use of Central Facilities.

Registry No. $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer), 70776-76-0; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2Me)\cdot(CF_2{=}CF_2)$ (copolymer), 68821-26-1; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Na salt, 90481-62-2; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) K salt, 90481-63-3; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Cs salt, 90481-64-4; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Ag salt, 90507-09-8; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Ba salt, 90481-65-5; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2H)\cdot(CF_2{=}CF_2)$ (copolymer) Mg salt, 90481-66-6; $(CF_2{=}CFOCF_2CF(CF_3)OCF_2CO_2^-)\cdot(CF_2{=}CF_2)$ (copolymer) Bu_4N^+ salt, 90507-12-3.

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Concerning the Origin of Broad Bands Observed in the FT-IR Spectra of Ionomers. Cluster Formation or Water Adsorption?

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ABSTRACT: Water immersion studies of ionomers derived from an ethylene–methacrylic acid copolymer have necessitated a reinterpretation of some of our previously published FT-IR results. The formation of clusters from multiplet structures was inferred from the broadening of the asymmetric carboxylate stretching vibration during annealing studies. However, it is demonstrated that broadening of this band can also be caused by the slow adsorption of water. Experiments performed under vacuum over fresh phosphorus pentoxide substantiate this hypothesis.

Introduction

Perhaps the most widely accepted model of ionomer superstructure is the multiplet–cluster concept advanced by Eisenberg.[1,2] This framework has dominated the interpretation of many vibrational spectroscopic studies to the extent that specific infrared bands and Raman lines have been separately assigned to multiplets or clusters. We were no exception to this general rule and our initial FT-IR studies of the sodium and calcium salts of ethylene–methacrylic acid copolymers were interpreted in terms of Eisenberg's model.[3,4] Specific sharp bands in the spectra of quenched films or films held at elevated temperatures (in the range 70–130 °C) were assigned to multiplets. Broad bands observed upon annealing these films for extended periods of time at room temperature were assigned to clusters. However, as a result of subsequent work on the salts of other group 1 and group 2 elements, we were forced to reevaluate these somewhat simplistic initial assignments.[5] Essentially, we used symmetry arguments to analyze the pattern of sharp bands in the spectra of freshly prepared films. On this basis, we postulated the existence of specific coordinated structures. Because infrared spectroscopy is principally sensitive to short-range order, the bands associated with such local structures should be characteristic of multiplets *and* any such assembly of multiplets in clusters. This revised interpretation left

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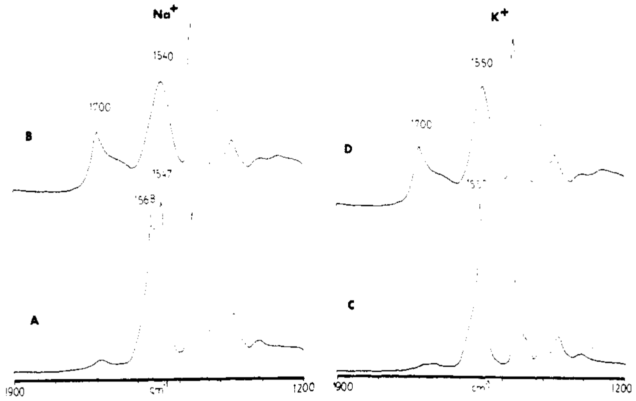

Figure 1. FT-IR spectra in the range 1900–1200 cm^{-1} of (A) the sodium ionomer quenched into liquid nitrogen from the melt, (B) the sodium ionomer after 39 days in water, (C) the potassium ionomer quenched from the melt, and (D) the potassium ionomer after 45 days in water.

dangling the assignment of the broad band observed upon annealing at room temperature.

One factor that must always be kept in mind when studying ionomers is the presence of water. Although we made extensive efforts to keep films in an anhydrous environment, a more thorough examination of the spectra of the annealed samples in the region 3100–3800 cm^{-1} showed multiple, weak, broad bands around 3300 cm^{-1}. It is well-known that bands in this region of the spectrum are indicative of hydrogen-bonded water molecules. This raised an important question: Can hydrated salt species be responsible for the band broadening observed during room-temperature annealing studies? In order to answer this question water immersion studies of the alkali metal, alkaline earth, and zinc salts were undertaken. The results of these studies are presented in this paper.

Experimental Section

The ethylene–methacrylic acid copolymer used in this study was obtained from E. I. du Pont de Nemours and Co. (Surlyn 1650) and was reported to contain 4.1 mol % methacrylic acid. The salts were prepared as described in previous papers.[3-5] To prepare films for infrared analysis each sample was pressed at 190 °C at 40000 psi several times and quenched in liquid nitrogen after each pressing. These films were thin enough to be within a range where the Beer–Lambert law is obeyed.[6] As in our previous studies, we are only concerned with completely neutralized ethylene–methacrylic acid copolymers with specific thermal histories. The absence of the carbonyl stretching bands at 1700 cm^{-1} (assigned to hydrogen-bonded acid pairs) and at 1750 cm^{-1} (attributed to lone acid groups) confirms that essentially complete neutralization has occurred.

Infrared spectra were obtained on a Digilab FTS-15B spectrometer. Two hundred scans at a resolution of 2 cm^{-1} were signal averaged and the spectra were stored on a magnetic disk system.

Results and Discussion

Alkali Metal Ionomers. Figure 1 shows the effect of water immersion upon the carboxylate stretching region of the infrared spectrum of the sodium and potassium ionomers. The spectral changes observed for the lithium and cesium ionomers are essentially the same as those of the sodium and potassium salts, respectively.

We have previously assigned the doublet occurring at 1568/1547 cm^{-1} in the sodium ionomer and at 1573/1548 cm^{-1} in the lithium ionomer to carboxylate stretching vibrations associated with octahedrally coordinated multiplets.[5] These bands appear prominently in samples quenched from the melt into liquid nitrogen, as illustrated by the spectrum shown in Figure 1A. Upon immersion of the film in distilled water (pH 7) for an extended period of time (46 days) at room temperature and subsequent removal of surface moisture, the spectrum of the sodium ionomer shown in Figure 1B is obtained. There are a number of important spectral changes. First, and most significantly, the well-resolved doublet at 1568/1547 cm^{-1} is replaced by a basically featureless broad band centered at 1540 cm^{-1}. Second, a new band at 1700 cm^{-1} is observed that is readily assigned to hydrogen-bonded carboxylic acid dimers. Close examination of the spectrum also reveals that there are also contributions from absorptions at approximately 1680 and 1590 cm^{-1}. These bands have been previously assigned to acid–salt complexes.[5] Interpretation of the above results appears reasonably simple. Upon immersion in water, a fraction of the metal cations exchanges with protons present in water to yield acid–salts and dimerized acid groups.

In contrast to the spectra of the sodium and lithium ionomers, analogous spectra of samples quenched from the melt containing the potassium and cesium ions are dominated by a surprisingly sharp singlet at 1550 and 1548 cm^{-1}, respectively. This is illustrated for the potassium ionomer in Figure 1C. This singlet has been assigned to localized multiplet structures that have a coordination number of eight. After water immersion, the spectrum of the film is remarkably similar to that of the sodium ionomer. The sharp singlet at 1550 cm^{-1} broadens considerably and there is the concurrent appearance of bands due to acid–salts and hydrogen-bonded acid dimers.

In addition to the changes observed in the carbonyl stretching region of the spectra of the alkali metal ionomers immersed in water, broad bands at approximately 3400 cm^{-1} are also detected. These bands may be confidently assigned to hydrogen-bonded water. It has been shown that water molecules will form complexes with salt species.[7] Incidentally, it was also noticed that crystallization of the ethylene portions of the copolymer chain occurs during the water immersion studies, as made evident by the splitting of the methylene rocking mode at 720/730 cm^{-1}. In fact, crystallization appears to develop more rapidly during water immersion compared to annealing at room temperature in air for the same period of time. We presume that chain mobility is increased due to water plasticization of the ionic domains.

Alkaline Earth Ionomers. A comparison of the spectra obtained from quenched and water-immersed samples of the alkaline earth ionomers (i.e., Mg, Ca, Sr, and Ba) reveals that the changes occurring within this group are very similar. We have chosen the strontium ionomer as a representative example, as shown in Figure 2. The 1542/1516-cm^{-1} doublet has been previously assigned to localized octahedrally coordinated multiplet structures, while the shoulder at 1560 cm^{-1} together with the band at 1680 cm^{-1} is indicative of acid–salts.[5] Upon water immersion, the well-resolved collection of bands between 1500 and 1600 cm^{-1} merge into a broad, asymmetrically skewed band centered at 1535 cm^{-1}. In addition, there is an enhanced absorbance at 1680 cm^{-1}. This would imply that upon water immersion, acid–salts are formed at the expense of the well-ordered multiplet structures. It is also important to note that there is little evidence for the formation of hydrogen-bonded acid dimers, which is in contrast to the analogous alkali metal ionomers and may be rationalized on the basis of relative strengths of the interactions between the cations and anions in the two groups.[7]

Zinc Ionomer. The zinc salt is unique among the different ionomeric materials that we have studied. Figure 3 shows that there is a slight broadening of the band at

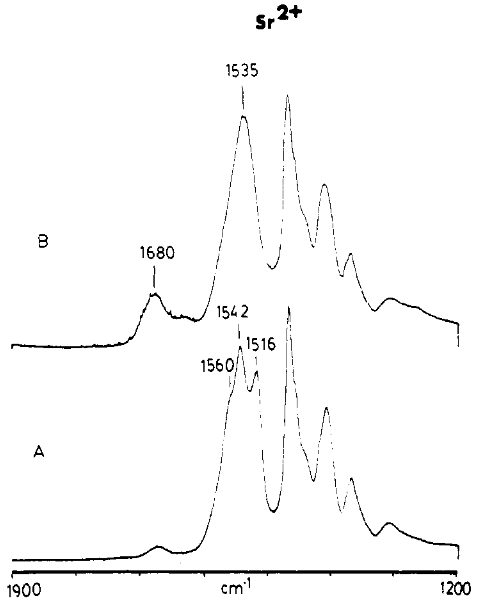

Figure 2. FT-IR spectra in the range 1900–1200 cm^{-1} of (A) strontium ionomer quenched into liquid nitrogen from the melt and (B) strontium ionomer after 21 days in water.

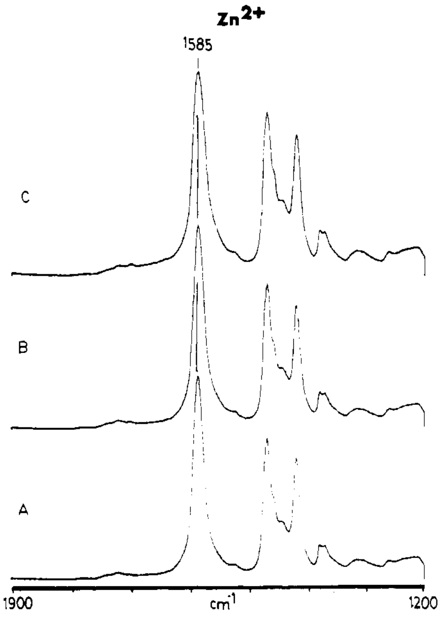

Figure 3. FT-IR spectra in the range 1900–1200 cm^{-1} of the zinc ionomer (A) quenched into liquid nitrogen from the melt, (B) after 4 days in water and (C) after 39 days in water.

1585 cm^{-1} after water immersion, but the spectra are, to all extents and purposes, identical. No evidence for the formation of acid–salts or hydrogen-bonded acid dimers is observed. We have previously shown that the single band associated with the asymmetric carboxylate stretching vibration of the zinc ionomer is consistent with a tetrahedrally coordinated multiplet structure.[5] Significantly, a tetrahedrally coordinated structure is electrically neutral, and it is reasonable to surmise that the zinc ionomer would therefore be less water sensitive. The spectral results appear to substantiate this hypothesis.

Cluster Formation or Water Adsorption? The above results cast serious doubts upon the original simple interpretation that the band broadening of the asymmetric carboxylate stretching vibration upon room-temperature annealing is due solely to cluster formation. The water immersion studies indicate that both acid–salts and dimerized acid groups (the latter especially in the group 1 salts) are formed (excluding the zinc ionomer). More importantly, the presence of water undoubtedly leads to a broadening of the asymmetric carboxylate stretching mode. It is therefore important to ask the following question: Were the results obtained during the room-temperature annealing studies fortuitous?;[3] in other words, are the observed effects due to a slow adsorption of water? If this is so, then how can we explain the annealing results obtained at elevated temperatures?[4] These questions will be addressed after the results of two critical sets of experiments are presented.

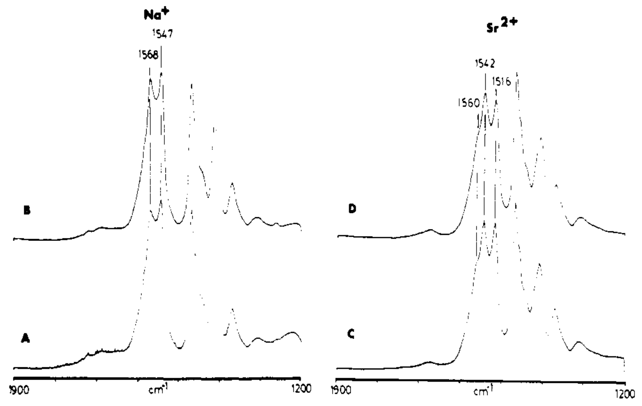

Figure 4. FT-IR spectra in the range 1900–1200 cm^{-1} of (A) the sodium ionomer quenched into liquid nitrogen from the melt, (B) the sodium ionomer after 89 days under vacuum over P_2O_5, (C) the strontium ionomer quenched from the melt, and (D) the strontium ionomer after 38 days under vacuum over P_2O_5.

Experiments Performed in Phosphorus Pentoxide in Vacuo. In order to essentially eliminate the complication of slow water adsorption during annealing at room temperature, quenched films of the ionomers were placed in small vacuum desiccators over fresh P_2O_5 which were then evacuated. (In our previous annealing study we had placed the samples in desiccators over anhydrous calcium sulfate.) Figure 4 compares representative spectra of the sodium and strontium ionomers quenched from the melt and after annealing for extended periods of time at room temperature under vacuum over fresh P_2O_5. There are no significant differences between the quenched and annealed samples. This strongly suggests that the broadening of the asymmetric carboxylate stretching vibration upon annealing, which we originally interpreted as evidence for cluster formation, was in fact due to the absorption of a small amount of water.

The final "nail in the coffin" is introduced when we consider the results of an experiment where a sample of the strontium ionomer was immersed in water for 1 day (Figure 5A) and subsequently placed over fresh P_2O_5 in a vacuum desiccator for 1 week (Figure 5B). Upon removal of the water from the film the characteristic doublet at 1542/1516 cm^{-1} associated with the localized multiplet structure reemerges.

Conclusions

There are several important cnclusions that arise from the studies presented in this paper.

1. There is little evidence to suggest that infrared spectroscopic studies of the carboxylate stretching region can be used to differentiate between multiplets and clusters. Our previous hypothesis,[3,4] which invoked band broadening of the asymmetric carboxylate stretching modes as multiplets aggregate to form clusters, appears moot. The original evidence on which this hypothesis was based included the elevated-temperature studies of the fully neutralized calcium and sodium salts where the bands

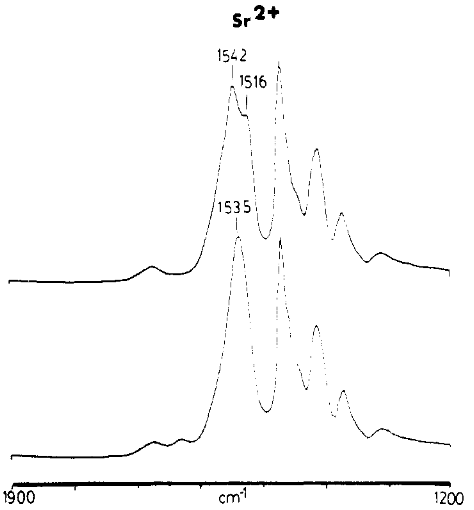

Figure 5. FT-IR spectra in the range 1900-1200 cm^{-1} of the strontium ionomer (A) quenched from the melt and immersed in water for 1 day and (B) after 1 week under vacuum over P_2O_5.

attributable to localized multiplet structures became better resolved and more distinct with increasing temperature. Although there was some theoretical justification that multiplets would be favored over clusters at elevated temperatures and, at that time, the infrared spectra in the hydroxyl stretching region suggested that water absorption was insignificant, it now appears that the elevated-temperature results may be explained in terms of a reduction of the concentration of water in the films upon raising the temperature.

Similarly, the long-term room-temperature, annealing results, which purported to show multiplet-to-cluster formation,[3] are now interpreted to be due to the slow adsorption of water into the films. Finally, we must reconsider the interpretation of the long-term annealing experiments performed at 80 °C.[4] A significant degree of crystallization of the ethylenic portion of the chains occurs at this temperature. In subsequently annealing this material at room temperature for extended periods of time, there is essentially no change in the spectra. (This is in marked contrast to the room-temperature annealing results of the quenched ionomer.) It was suggested that the development of crystallinity, formed by annealing at 80 °C, "freezes in" the "favored" multiplets structure and that the multiplet-to-cluster transformation at room temperature is prevented by the crystallites. Given the results presented in the current paper, we require an alternative explanation. It is feasible that the presence of the crystalline domains formed at 80 °C significantly reduces the rate of diffusion of water into the film at room temperature. Although plausible, we consider this to be somewhat speculative.

Eisenberg[2] has previously observed that studies on ethylene-methacrylic acid ionomers indicate that clusters are the only ionic species present and that single multiplet structures do not occur even at very low ion concentrations. If this observation applies to our essentially fully ionized samples then we must conclude that multiplets retain their structural integrity within clusters.

2. Water absorption obviously plays an important role in the overall structure on ionomers. However, different salts are affected to different degrees. Not only does hydration of the ionic domains occur, but water also is instrumental in the formation of acid-salts. Hydration and acid-salt formation leads to a broadening of the asymmetric carboxylate stretching vibration. The zinc ionomer appears to be the least affected by the water for reasons stated in the text.

Acknowledgment. We acknowledge the financial support of the National Science Foundation, Grant DMR-8206932, Polymers Program.

Registry No. (Ethylene)·(methacrylic acid) (copolymer) sodium salt, 25608-26-8; (ethylene)·(methacrylic acid) (copolymer) potassium salt, 26376-80-7; (ethylene)·(methacrylic acid) (copolymer) strontium salt, 88496-05-3; (ethylene)·(methacrylic acid) (copolymer) zinc salt, 28516-43-0; H_2O, 7732-18-5.

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Small-Angle Scattering of Polyelectrolyte Solutions

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ABSTRACT: The small-angle scattering intensity of polyelectrolyte solutions is calculated, assuming a wormlike chain polymer model. The calculation assumes that the probability of finding two monomers of different polymers within a distance R_0 is negligible because of strong electrostatic repulsion between the polyelectrolyte chains. The scattering intensity becomes a monotonically decreasing function of q for small R_0, but it has a broad maximum for large R_0 (q is the absolute value of the scattering vector). The maximum point q_m and the maximum intensity per monomer at q_m are approximately proportional to the square root of the monomer concentration and to its reciprocal value, respectively. The calculated values of q_m agree well with those of the small-angle neutron scattering of deuterated sodium poly(styrenesulfonate) solutions without added salts obtained by Nierlich and others. The result of the maximum intensity also agrees qualitatively with that experiment.

I. Introduction

The small-angle neutron and X-ray scattering curves of polyelectrolyte solutions have various characteristic forms according to the physical conditions,[1-4] and particularly with no added salts they have a broad peak in the region $q = 10^{-2}$–10^{-1} Å^{-1}, where q is the absolute value of the