

Poly(methyl methacrylate) Based Ionomers. 1. Dynamic Mechanical Properties and Morphology

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ABSTRACT: A new type of amorphous ionomer based on poly(methyl methacrylate) (PMMA) was prepared. Dynamic mechanical thermal analysis (DMTA), coupled with some differential scanning calorimetry (DSC), was used to study the morphology of the PMMA-based ionomers. Results obtained are compared with those determined for poly(styrene-co-metal methacrylate) ionomers and are discussed in terms of multiplet-cluster models. Characteristic behavior common to amorphous ionomers was observed for the PMMA-based ionomers: two primary relaxations appeared for ionomers with high ion contents, with glass transition temperatures (T_g) increasing with ion content and the rubbery modulus increasing significantly. Within the ion content range studied, the matrix T_g increased at a rate of ca. 6 °C/(mol %), in contrast to ca. 3 °C/(mol %) for the PS ionomer. At a critical ion content of about 12 mol %, an ion-rich cluster phase dominates over the ionic multiplet-containing (matrix) phase. It was also found that the secondary (β)-transition peak, reflecting the local motion of the side groups of PMMA, was spread into two in PMMA ionomers, which reflect two different environments corresponding presumably to the cluster phase and the matrix phase. Both of these secondary relaxation peak positions increased with ion content. It was observed that the divalent counterion calcium created stronger intermolecular interactions than the monovalent counterion sodium.

Introduction

Ionomers are ion-containing polymers having a small amount (usually up to 10–15 mol %) of ionic groups along nonionic backbone chains. One of the earliest ionomers is based on poly(butadiene-co-acrylonitrile-co-acrylic acid), introduced by B.F. Goodrich as an ionic elastomer in the early 1950s.¹ In the mid-1960s, DuPont introduced Surlyn, a family of ionomers based on poly(ethylene-co-methacrylic acid), which possesses remarkable clarity and superior mechanical properties.^{2,3} The commercial success of Surlyn resins was an important factor that stimulated the research of ionomers. Since then, a variety of ionomers have been developed. Because of the significant changes in physical properties due to the formation of ionic aggregates, such as high melt viscosity, increased glass transition temperature, and enhanced mechanical properties, ionomers have been studied extensively during the past 2 decades.^{4–15} Although numerous research publications, including many monographs and review papers, have been published, the structure of ionomers is still not fully understood. To explain the significant changes in physical properties caused by ionic interactions, many models for the morphology of ionomers have been proposed. These have been reviewed recently by Eisenberg et al.¹² and Mauritz.¹³ The multiplet-cluster concept¹⁶ has been most frequently used to explain various experimental results. The fundamental structural entity is a contact ion pair, and ionic aggregates called multiplets made of only a small number of ion pairs can be formed without the involvement of organic backbone chains. The Coulombic interaction between these multiplets may favor further aggregation into clusters as a second phase in the multiplet-containing matrix at higher ion content. The elastic force from entropy considerations of local chain extension opposes clustering. Organic backbone chains as well as many ion pairs are involved in cluster formation. Recent

models proposed by Forsman,^{17,18} Dreyfus,¹⁹ and Dayte and Taylor²⁰ have reached conclusions similar to those of the Eisenberg model.

To study ionomer morphology, two techniques have been most widely used: dynamic mechanical thermal analysis (DMTA) and small-angle X-ray scattering (SAXS). DMTA gives information on the relaxation of molecular motions, which are sensitive to the structure of polymers. The DMTA data most extensively studied are those of polystyrene-based ionomers, such as poly(styrene-co-metal methacrylate)^{21–23} and the salt form of partially sulfonated polystyrene.^{24–26} Since these ionomers are amorphous, all the changes observed in DMTA data reflect morphological changes arising from ionic interactions. It has been shown that storage moduli (both glassy and rubbery) increase with increasing ion content. The glass transition temperature increases with increasing ion content, due to the ionic cross-linking effect by ionic aggregates. Probably, most significant are the results showing the appearance of a high-temperature relaxation peak in addition to the usual T_g peak: with increasing ion content, the low- T_g peak height reduces, while the high- T_g peak increases and eventually dominates the entire relaxation behavior. This has been used as evidence for the formation of an ionic cluster phase. The low-temperature peak reflects the matrix phase containing multiplets, and the high-temperature peak reflects the ion-rich phase (cluster phase). Although there are controversies with respect to the nature of the high-temperature peak, it seems to be a glass transition with a high activation energy.^{22,23} Nevertheless, the DMTA results clearly indicate the two-phase nature of ionomers, as seen for other multiphase polymers, such as block copolymers and immiscible polymer blends.²⁷

In contrast to DMTA, which reflects both ionic and nonionic structures of the ionomer, SAXS has been used to study ionic aggregate structures. Cooper and co-workers^{28–30} have conducted extensive SAXS work and have proposed a “hard-sphere” model. This model

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attributes the SAXS ionomer peak, typically observed in intensity vs scattering angle curves for ionomers, to interparticle scattering of "hard spheres" made of ionic aggregates, which are distributed more or less randomly with a liquidlike order. Although the model is in excellent agreement with the entire SAXS profile,²⁸ this model cannot account for the two-phase behavior suggested by dynamic mechanical measurements of ionomers. MacKnight and co-workers proposed a "core-shell" model.³¹ This model postulates the existence of clusters with a radius of 8–10 Å (ca. 50 ion pairs), which are shielded from the surrounding matrix ions by a shell of hydrocarbon chains on the order of 20 Å thick. The model attributes the SAXS peak to intraparticle scattering; i.e., the overall thickness of the cluster with an organic shell is considered to correspond to the SAXS peak position. Although this model can explain scattering from clusters (not multiplets), it is not consistent with SAXS results on halato-telechelic ionomers, which also show an ionomer peak but give no indication of cluster formation.³²

To reconcile the discrepancies in DMTA and SAXS results, Eisenberg et al. proposed a new multiplet-cluster model (EHM model)¹² by revising his classical multiplet-cluster model¹⁶ according to recent experimental results.^{22,33} In this new model, the multiplet has the same meaning as in the classical model, i.e., an aggregate of only several ion pairs. The formation of multiplets (not cluster) depends on the competition between electrostatic interactions among ion pairs and the elastic forces of the chains to which the ionic groups are attached. Low dielectric constant and T_g of the host polymer favor the aggregation because of strong Coulombic interaction and weak elastic restriction. Each ion pair in a multiplet anchors the polymer chain at the point to which it is attached; therefore, the mobilities of the polymer chains in the vicinity of the multiplets are considered to be reduced. It is envisaged that each multiplet is therefore surrounded by a layer of polymer chains with reduced mobility. Since the thickness of the region of restricted mobility surrounding a multiplet is determined largely by the flexibility of the polymer backbone chain, the EHM model assumes that this thickness is on the order of the persistence length of the polymer. Although the restricted regions are too small to be considered as a second phase having their own T_g , they can effectively increase the T_g of the polymer by working as large cross-links. As the ion content increases, the average distance between multiplets decreases, and eventually some overlap of restricted mobility regions surrounding multiplets occurs. When this overlap becomes more frequent, large enough contiguous regions (>50–100 Å in diameter) of restricted mobility can be formed to have their own T_g . Such an overlapped contiguous region with its own separate T_g constitutes a cluster, which can explain the two-phase morphology suggested by dynamic mechanical data. The SAXS "ionic peak" arises from the interparticle scattering of the multiplets (corresponding to the distance between centers of multiplets). The EHM model reconciles SAXS and DMTA data and provides an explanation for phase inversion at relatively low ion contents. It is also consistent with a wide range of experimental data for random ionomers.¹²

To avoid complexities arising from crystallinity and to study the effect of ionic interactions on the ionomer morphology directly, most models of ionomers are compared with experimental data from amorphous ionomers. Most widely used ionomers are polystyrene

(PS) based ionomers. In this work, we investigate another type of amorphous ionomer based on poly-(methyl methacrylate) (PMMA). DMTA is used to investigate relaxation behavior and morphology of the PMMA-based ionomers. By comparing the results obtained with data for another amorphous ionomer, we can check the generality of the conclusions, such as the applicability of the multiplet-cluster model, drawn mainly from the results on PS ionomers. In addition, since the T_g s of PS and PMMA are essentially identical (ca. 100 °C) and both are based on amorphous backbone chains, the effect of differences in the two base polymers, such as chain flexibility and dielectric constant, can be discussed. Since PMMA is a widely used thermoplastic polymer with excellent optical clarity and better impact strength than PS, we can also expect better properties for PMMA ionomers than for PS ionomers.³⁴

Experimental Section

Preparation of Ionomers. Two methods were used to prepare PMMA-based ionomers according to ion content: hydrolysis of PMMA and random copolymerization of the component monomers. Low ion content (0.8 mol %) ionomers were prepared by the hydrolysis of PMMA with NaOH in THF/H₂O (50/50, v/v) through refluxing. The PMMA, with a weight-average molecular weight of ca. 100 000, was obtained from Polysciences, Inc. The ionomer samples were recovered by precipitation of the reaction mixture into methanol and then washed five times with methanol. The samples were dried under vacuum at 70 °C for 48 h. The dried samples were redissolved in benzene/methanol (90/10, v/v) and freeze dried. The ionomer samples were initially obtained as a sodium salt form. They were converted to acid form to determine the ion content by titration. Precisely weighed ionomers (0.1 g each) were dissolved in THF/H₂O (90/10, v/v). The ionomer solution was passed through an ion-exchange resin (Amberlyst-15; Rohm and Haas Co.) column, which was conditioned and washed with solvent in advance. Then, the column was washed with a solvent of 5 times the volume of the solution to make sure that all the polymer molecules passed through the column. The collected solution was concentrated by evaporation of solvent under vacuum at 30–40 °C. The concentrated solution was then titrated with a NaOH solution (in THF/H₂O (50/50)) with phenolphthalein as an indicator.

The Ca ionomers with low ion content were prepared from the corresponding low ion content Na ionomers. The Na ionomer sample dissolved in benzene/methanol (90/10, v/v) was poured into an excess amount of a dilute HCl solution (approximately 100 times as much as needed). The mixture was heated while stirring to evaporate the organic solvents (benzene and methanol). At about 80 °C (the boiling point of benzene), the acid form copolymer was precipitated as a white foam. The washed and dried foam was milled into powder and washed again with deionized water five times to remove the remaining HCl. The dried powder was redissolved in benzene/methanol (90/10, v/v) and neutralized with an excess amount (3 times as calculated) of a Ca(OH)₂/H₂O solution (4×10^{-2} N). The two-phase reaction mixture was vigorously stirred overnight. The calcium ionomer was precipitated from methanol, redissolved into benzene/methanol (90/10, v/v), and freeze dried.

The ionomer samples with higher ion contents (6.0, 12.4, and 24.7 mol %) were prepared by the neutralization of random copolymers of methyl methacrylate and methacrylic acid with sodium hydroxides. The copolymers were products (Polysciences, Inc.) of free-radical bulk copolymerization at 60 °C with AIBN initiator.^{35a} The ion contents were determined by titration of the acid copolymers in benzene/methanol (90/10, v/v) with a methanolic NaOH solution. The exactly neutralized ionomer solutions were freeze dried, followed by vacuum drying for 7 days.

Poly(styrene-co-methacrylic acid) samples were prepared in connection with other projects; details of the synthesis are

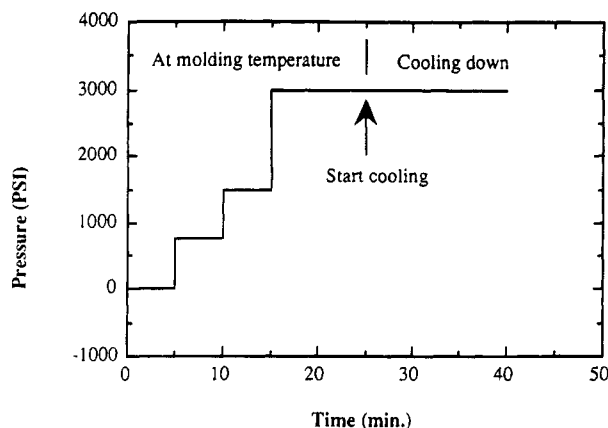


Figure 1. Compression-molding process.

Table 1. Compression-Molding Temperatures of Specimens for Dynamic Mechanical Thermal Analysis

sample	molding temp (°C)	releasing temp (°C)
PMMA	200	80
MMA-0.8%MAA-Na ^a (Ca)	215	85
MMA-6.0%MAA-Na	225	85
MMA-12.4%MAA-Na	240	100
MMA-24.7%MAA-Na	290	120
PS	160	80
S-5.5%MAA-Na ^b	220	85
S-8.2%MAA-Na	260	85

^a Poly(methyl methacrylate-co-sodium methacrylate). ^b Poly(styrene-co-sodium methacrylate).

described elsewhere.^{35b} The neutralization and the freeze drying processes were the same as those in the preparation of PMMA-based ionomers (greater than 1 mol %) as described above.

Dynamic Mechanical Thermal Analysis (DMTA). All specimens were made by compression molding according to a process shown in Figure 1. Sufficient amounts of powder or bead sample were transferred into a preheated mold made of aluminum foil between two flat copper plates. The molding temperatures are listed in Table 1. The applied pressure was increased step by step. After keeping the pressure at 3000 psi for 10 minutes; the mold was cooled down with cooling water under the constant pressure. The pressure was released at the releasing temperatures also listed in Table 1. The specimens were cut to dimensions of 0.5 × 2.5 × 12 mm and polished with Nos. 400, 600, and 0000 emery papers, in this order. A piezotron (Rheograph Solid, Toyoseiki, Japan) was used to conduct dynamic mechanical thermal analysis. The frequency was 1 Hz, and the heating rate was 4 °C/min. Starting temperatures were room temperature for the primary relaxation peak observation and -50 to 100 °C for the secondary relaxation peak observation. The details of the DMTA measurements are described elsewhere.²⁴ All data are shown by continuous curves rather than individual data points, since many data points are collected: typically at the interval of 1 °C.³⁶

Differential Scanning Calorimetry (DSC). DSC measurements were conducted with a 910 differential scanning calorimeter (DuPont Instruments). The heating rate was programmed to be 10 °C/min, starting usually from room temperature. The sample chamber was flushed with a steady flow of N₂ gas at a rate of 50 mL/min. To eliminate the effect of sample thermal history, each sample weighing 5–10 mg was run twice. After the first run, the sample was quenched to room temperature with liquid N₂. The thermograms of the second run were used for analysis. The glass transition temperatures were determined by the intersection method.

Results and Discussion

Ion Content Effect on Storage Moduli. The primary transitions discussed here are the glass transi-

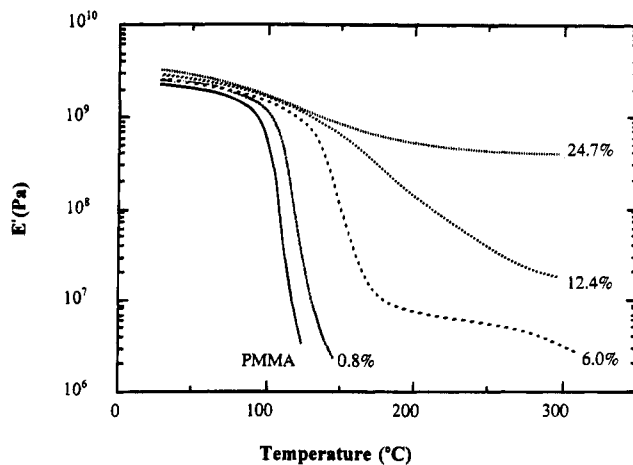


Figure 2. Storage modulus versus temperature for PMMA ionomers (Na salt) with various ion contents.

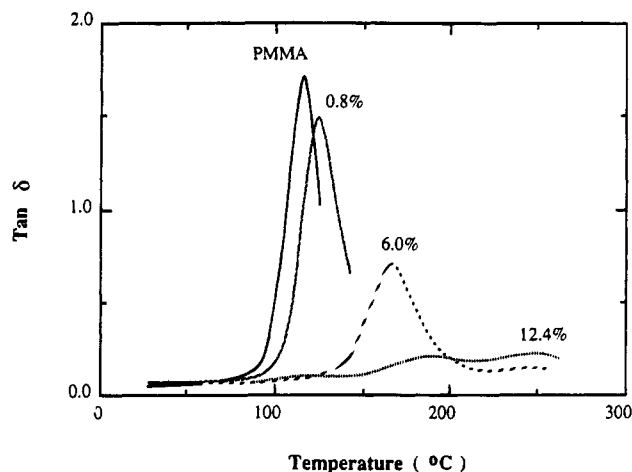


Figure 3. Loss tangent versus temperature for PMMA ionomers (Na salt) with various ion contents.

tions corresponding to the temperatures at which main-chain segmental motion is effectively frozen. For PMMA and the PMMA-based ionomers, the temperature range including these transitions is far above room temperature (> 100 °C). The DMTA results for the PMMA-based ionomers are shown in Figures 2 and 3. Figure 2 is a plot of storage modulus against temperature for sodium ionomers having various ion contents. Figure 3 is a plot of loss tangent ($\tan \delta$) against temperature for the sodium ionomers.

Figure 2 indicates that the modulus in the entire temperature range increases with ion content. Especially, the rubbery modulus³⁷ increases significantly. These results are basically similar to those obtained for PS-based ionomers.^{21–26} The glassy moduli at 30 °C of the ionomers are plotted against ion content in Figure 4, indicating that the glassy modulus increases linearly with ion content.

The rubbery moduli of the ionomers, chosen as the moduli at the intermediate temperature of the two glass transition temperatures of the ionomers, are plotted in Figure 5. The theoretical values calculated from rubber elasticity theory³⁸ are also plotted in Figure 5 with the assumption that all the ion pairs are involved in effective cross-links. The effect of molecular entanglements of backbone chains is also included in the calculation.

The effect of covalent cross-linking on physical properties has been widely studied.^{39–44} Comparing the

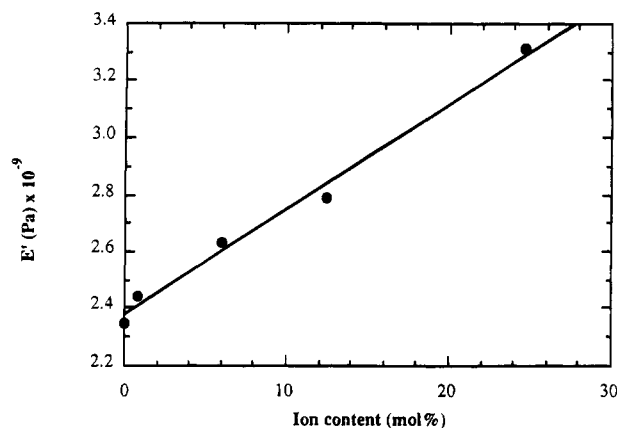


Figure 4. Glassy modulus (30 °C) versus ion content for PMMA ionomers (Na salt).

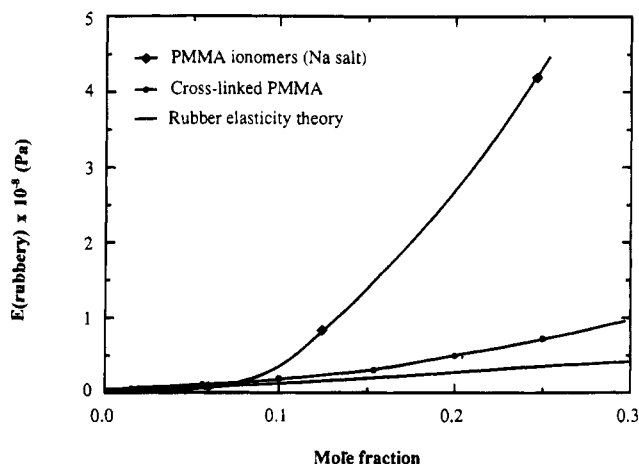


Figure 5. Comparison of rubbery moduli of PMMA-based ionomers with those of covalently cross-linked PMMA and from rubber elasticity theory.

effects of covalent cross-linking and ionic cross-linking can provide some insight into the nature of ionic aggregates. The results of covalently cross-linked PMMA obtained by Tobolsky et al.⁴¹ are also plotted in Figure 5. Both ionic cross-linking and covalent cross-linking are in general agreement with rubber elasticity theory at low cross-link density, whereas at high cross-link density, rubber elasticity theory is not applicable anymore; elastic moduli from both ionically cross-linked PMMA (ionomers) and covalently cross-linked PMMA are higher than the theoretical values. For a given number of bonds (cross-links), covalently cross-linked PMMA is expected to have a higher modulus than that of ionically cross-linked PMMA, since some of the ion pairs may exist as isolated ion pairs.²⁴ The experimental results are just the opposite—the modulus of ionically cross-linked PMMA is higher than that of covalently cross-linked PMMA. According to the multiplet-cluster model,^{12,16} an ion-rich second phase made of clusters is formed at high ion content; therefore, clusters are more effective to enhance the rubbery modulus than either the multiplet-containing matrix or covalently cross-linked polymers. The more effective increase in the rubbery modulus by cluster formation compared with multiplet formation is well-known for PS-based ionomers.^{5,21–26,45} This is attributed to the second-phase nature of ionic clusters, which may also act as reinforcing fillers. Kim et al.²³ successfully used a modified Guth equation for the poly(styrene-co-sodium methacrylate) ionomers to consider the filler effect of ionic clusters, where the volume fraction of the filler (cluster)

Table 2. Primary and Secondary Transition Temperatures of PMMA Ionomers (Na Salt), Determined from DSC and Dynamic Mechanical Thermal Analysis

ion content (mol %)	T_g (DSC) (°C)	T_{g1} (DMTA) (°C)	T_{g2} (DMTA) (°C)	$T_{\beta 1}^a$ (°C)	$T_{\beta 2}^a$ (°C)
0.0	97	113		20	
0.8	103	124		no data ^b	no data ^b
6.0	147	163	244	37	85
12.4	177	183	254	50	112
24.7					124

^a With an accuracy of ± 10 °C. ^b Low-temperature data, starting from -50 to -100 °C, are not available.

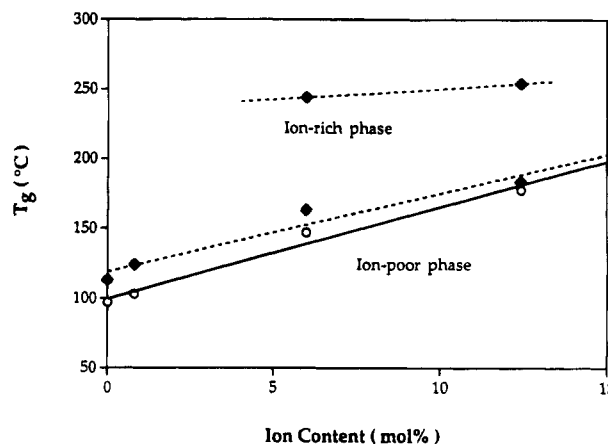


Figure 6. Glass transition temperatures of PMMA ionomers (Na salt) versus ion content: DMTA data (dashed lines) and DSC data (solid line).

is evaluated from the area under the $\tan \delta$ curve. Although such an approach may be useful for the PS ionomers, we did not conduct such an analysis for the PMMA ionomers, since the volume fraction of the cluster phase is difficult to estimate due to the decrease of the total area under the $\tan \delta$ curve.⁴⁶

Ion Content Effect on Glass Transition Temperatures. The glass transition temperatures of PMMA-based ionomers (sodium salt) are listed in Table 2. Figure 6 is a plot of both glass transition temperatures against the ion content of these ionomers. The matrix glass transition temperature of the ionomers, T_{g1} , determined from the $\tan \delta$ peak position in DMTA data, increases linearly with ion content, with an increase rate of 5.5 °C/(mol % ion content). The line is drawn according to the least-squares method. This value is higher than that of polystyrene-based ionomers: both sulfonated PS ionomers and poly(styrene-co-sodium methacrylate) ionomers show a rate of increase of ca. 3 °C/(mol % ion content).^{5,24} Therefore, PMMA ionomers may be more effective than PS ionomers in enhancing the usable temperature range. According to the new multiplet-cluster model, ionomers derived from polymers with more flexible chains are expected to have a lower rate of increase of T_g than ionomers derived from less flexible polymers.¹² However, this is not the case for our system. More work needs to be done to explain this discrepancy.

It should be added that studies of PMMA-based ionomers as hydrocarbon ionomer membranes were reported recently by Gronowski et al.⁴⁷ They also noted an increase in T_g with ion content. However, their results show some differences from ours: no high T_g peaks, corresponding to a cluster T_g , were observed and the storage modulus versus temperature curves only shifted to higher temperature with ion content.⁴⁷ They

attributed these discrepancies to the difference in counterions (Cs in their studies and Na in our work); Cs salts are more difficult to cluster because of the larger size of the Cs counterion. Also, the possible effect of water in disrupting the clusters was mentioned. Their samples were obtained by precipitation into water, followed by vacuum drying at 160 °C for 2 days prior to molding, while our samples were freeze-dried in benzene/methanol (90/10, v/v), followed by vacuum drying for 1 week; therefore, it is likely that the amount of water, if any, was higher in the precipitated samples than in the freeze-dried samples. It is known that PMMA can absorb an appreciable amount of water from the environment, and this can have a significant effect on physical properties.^{34,48}

Phase Inversion Phenomenon. On the basis of the analysis of loss tangent ($\tan \delta$) data for poly(styrene-co-alkali methacrylate) ionomers, Hird and Eisenberg²² found that the sum of the areas under the two glass transition peaks (corresponding to ion-poor and ion-rich phases) is relatively constant for all the ionomer samples. This suggests that each phase in PS-based ionomers makes a similar contribution to the overall loss tangent data based on its weight fraction²² or volume fraction.¹² On the basis of these observations, they plotted the areas corresponding to a matrix T_g and a cluster T_g as a function of ion content and found that the cluster phase dominates over the matrix phase above the critical ion content of 6 mol %. Although the value of $\tan \delta$ is not necessarily a reflection of the volume or weight of a certain phase, it is a common observation that the relative volume fraction or weight fraction of a given phase is higher when its peak value or area under the peak is higher.⁴⁹ This can be qualitatively understood because the higher the fraction of a certain phase in a multiphase system, the more moving units of that phase contribute to the response.

Although it may be naive to evaluate from loss peak heights or areas the contribution of each phase for ionomers of high ion content, which shows two relaxation mechanisms having different activation energies, it is still useful to compare qualitatively values obtained for different ionomers; therefore, we have analyzed loss tangent data for the PMMA-based ionomers. It seems that the sum of the area under the loss tangent peaks is not a constant but decreases with increasing ion content, as seen in Figure 3. Chang et al.⁵⁰ also found that the area under the loss tangent peak decreased with increasing cross-link density for poly(methyl acrylate), a result similar to ours for the PMMA-based ionomers. The peak height values of loss tangent ($\tan \delta$) versus ion content are plotted in Figure 7 for the PMMA-based sodium ionomers. As the ion content increases, the peak height of the multiple-containing matrix phase (ion-poor phase) decreases, while the peak height of the cluster phase (ion-rich phase) increases. At ca. 12 mol % ion content, the ion-rich phase becomes dominant over the ion-poor phase. This critical ion content of ca. 12 mol % is much higher than that of PS-based ionomers (ca. 6 mol %). The higher critical ion content for the PMMA-based ionomers can be explained on the basis of both the classical and the new multiplet-cluster models.

According to the classical model, it is a result of the difference in dielectric constants.^{5,16} The ionic interaction between ionic entities is inversely proportional to the dielectric constant of the medium; hence, it is expected that the higher the dielectric constant of the

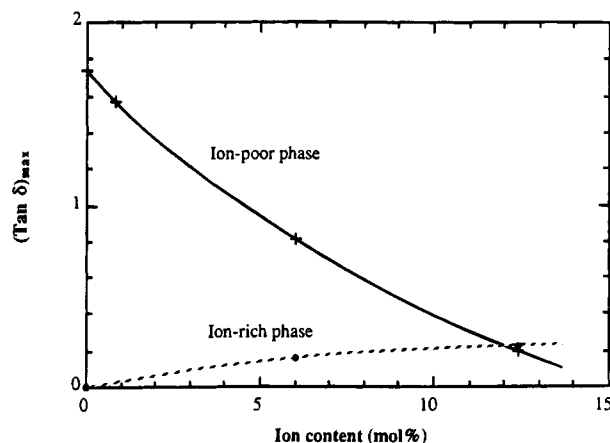


Figure 7. Loss tangent peak height versus ion content for ion-poor phase and ion-rich phase of PMMA ionomers (Na salt).

polymer matrix, the less the tendency at any given ion content for the multiplets to coalesce to form ionic clusters. Because PMMA has a higher dielectric constant ($\epsilon = 3.0$) than PS ($\epsilon = 2.5$),⁵¹ a higher ion content is required to reach the critical value. The high value (12–16 mol %) reported for poly(ethyl acrylate) (PEA) ionomers ($\epsilon = 3.5$ –5) is explained in a similar fashion.^{5,52}

According to the new multiplet-cluster model,¹² another explanation is possible. In this model, the flexibility of the backbone chains of ionomers plays an important role. It is suggested that there is a layer of restricted chain mobility surrounding each multiplet with a radius about the size of the persistence length. To form the ionic cluster phase, the multiplets with surrounding restricted layers must be close enough to each other so that overlap of the restricted layers can occur. Therefore, ionomers made of flexible parent polymers are expected to form clusters at a higher ion content than that of ionomers made of less flexible parent polymers. It is known that atactic PMMA chains are more flexible than atactic PS chains: for example, the persistence length of PMMA is 7.2 ± 0.5 Å (21 °C), while the persistence length of PS is 9.1 ± 0.2 Å (25 °C).⁵¹ Suppose that the critical ion content is determined by the volume fraction of the restricted chain mobility regions. If we assume that all the multiplets are around 3 Å in radius, according to the new multiplet-cluster model, the volume of a multiplet in a PS based ionomer is ca. 1.7 times that in a PMMA based ionomer. According to the new model, the dielectric constant of the polymer has an effect on the formation of the multiplets. PS has a lower dielectric constant so that there will be a stronger interaction between contact ion pairs in PS ionomers. With this correction, the volume fraction of the restricted mobility regions in a PS-based ionomer could be even closer to 2 times that in the PMMA-based ionomer with the same ion content. With this analysis, it is not surprising that the critical ion content of PMMA-based ionomers is about twice that of PS-based ionomers.

Figure 8 is a magnified plot of $\tan \delta$ versus temperature for the two high ion content PMMA ionomers (12.4 and 24.7 mol %). For the 12.4 mol % ionomer, two glass transition peaks are clearly identified (183 and 254 °C). For the 24.7 mol % ionomer, both peaks seem to disappear. The disappearance (or negligibly small contribution) of the first peak may indicate that most of the polymer chains are involved in the cluster phase

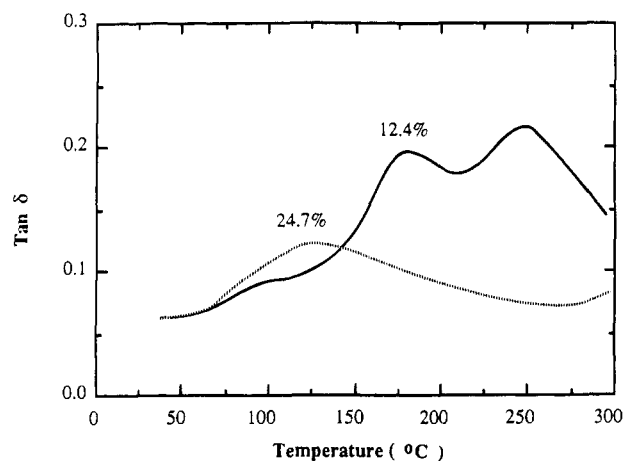


Figure 8. Loss tangent versus temperature for PMMA ionomers (Na salt) with high ion contents.

(ion-rich phase) at such a high ion content—no more ion-poor phase. It has recently been reported that PS ionomers with very high ion contents show essentially only the high- T_g peak, because most of the polymer chains are in a cluster phase.²³ For the 24.7 mol % PMMA ionomer, the second glass transition peak, associated with onset of mobility in the cluster phase, “should” not disappear. However, as the transition temperature increases with increasing ion content, it is believed that the cluster transition peak has been shifted to a temperature higher than or overlapping with the decomposition temperature so that it cannot be detected. The loss peak at 124 °C for the 24.7 mol % ionomer and the low intensity peak at around 100 °C for the 12.4 mol % ionomer are believed to be secondary transition peaks, as will be discussed in detail later.

Effect of Counterions on Dynamic Mechanical Properties. It has been observed that, for 4.1 mol % sulfonated polystyrene ionomers, samples containing divalent Ca ions had a fatigue lifetime almost 3 times that of specimens containing monovalent K or Cs ions.⁵³ It has also been found that the divalent Ca ionomer shows a much more extended rubbery plateau region than the monovalent K and Cs ionomers.²⁴ This is believed to be an indication of higher strength of ionic interactions and higher stability of ionic aggregates in divalent Ca ionomers than in monovalent ionomers.

To study the effect of counterion on the strength and stability of ionic association in PMMA-based ionomers, both sodium and calcium salts, having an ion content of 0.8 mol %, were prepared. Figure 9 shows that the Ca ionomer has a more extended rubbery plateau than the corresponding Na ionomer. This is an indication that intermolecular interactions through association with divalent Ca ions are stronger than those through ion pair interactions among monovalent Na ionomers. However, both sodium and calcium ionomers have the same modulus-temperature curve in the glassy region and in the glass transition region. Figure 10 is a plot of loss tangent ($\tan \delta$) versus temperature for the 0.8 mol % Ca ionomer, the corresponding Na ionomer, and their parent polymer PMMA. These figures show that the Ca ionomer and the Na ionomer have the same glass transition temperature, which is higher than that of the parent PMMA.

Figure 10 also shows that, for the Ca ionomer, there appears to be a high-temperature relaxation peak, usually assigned to an ionic cluster phase, and that the height of the $\tan \delta$ peak (or the area under the peak) of

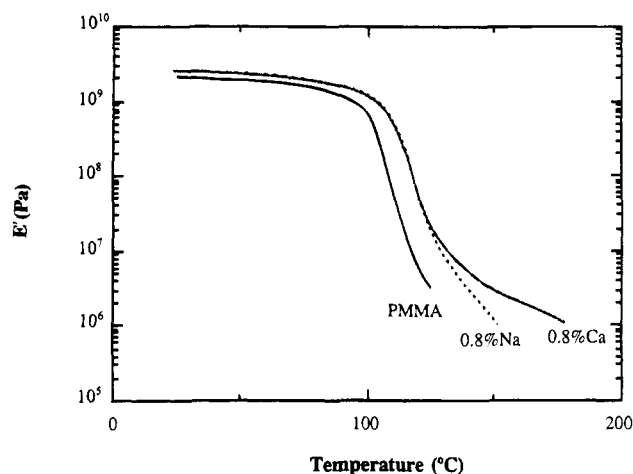


Figure 9. Storage modulus versus temperature for PMMA-based sodium and calcium ionomers with ion content of 0.8 mol % as well as PMMA.

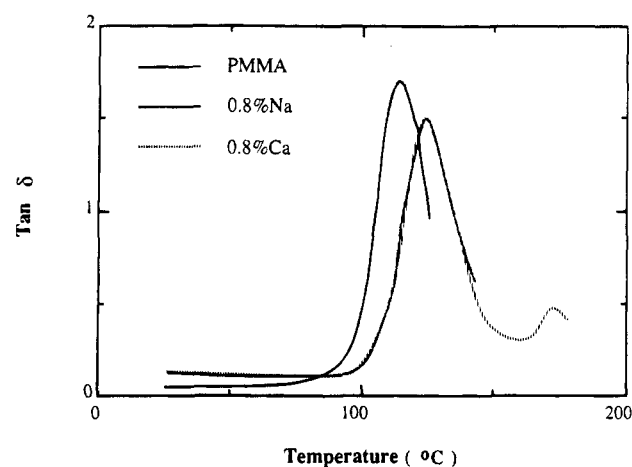


Figure 10. Loss tangent versus temperature for PMMA-based sodium and calcium ionomers with ion content of 0.8 mol % as well as PMMA.

the principal glass transition, which is smaller than that of PMMA, has the same values for both the Na and Ca ionomers. Eisenberg et al.^{12,22} indicated, from results on PS-based ionomers, that the area under a loss tangent peak was proportional to the volume fraction of the corresponding phase and that the sum of the areas under the peaks was constant. For PMMA-based ionomers, this does not seem to be the case as discussed earlier. However, it is probably true that phases with the same volume fraction and similar structure (such as the ion-poor phases in the low ion content Na ionomers and Ca ionomers) have the same $\tan \delta$ peak value (or the same area under the peak). It is also possible that the 0.8 mol % Na ionomer has not formed an ion-rich phase, probably because the ion pair association including monovalent Na ions at such a low ion content is too weak to withstand the molecular motion above T_g , unlike the association involving divalent Ca ions.

Secondary Transitions of PMMA Ionomers. So far, we have discussed the effects of ionic associations on glass transition temperatures of PMMA-based ionomers. There have been many reports about the effects of ionic interactions on glass transitions (primary or α transitions) for ionomers. In contrast, little work has been reported on the effects of ionic interactions on secondary transitions.^{7,25} In PMMA there is a secondary relaxation, β -transition, which is attributed to the

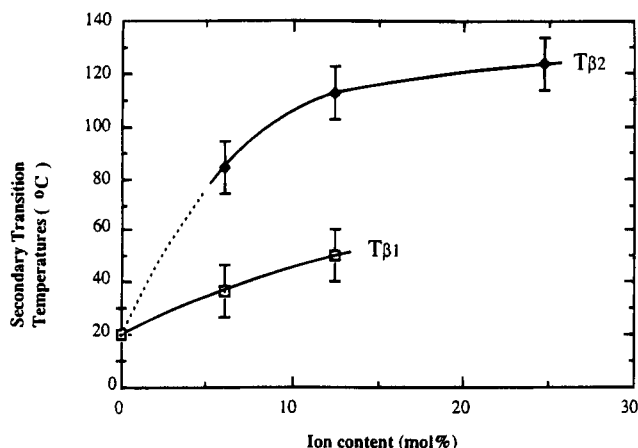


Figure 11. Secondary transition temperatures of PMMA ionomers (Na salt) versus ion content.

rotation of the methoxycarbonyl side group ($-\text{COOCH}_3$) around the C—C link that connects the side group with the main chain.^{54,55} The β -transition temperature of PMMA measured in this study is 20 °C, which is close to the value reported (25 °C) by Heijboer.⁵⁴

In Figure 8, it was noted that transition peaks (below the primary transition) were present for the PMMA-based sodium ionomers having ion contents of 12.4 and 24.7 mol % and that the peak temperature of the 24.7 mol % ionomer was higher than that of the 12.4 mol % ionomer. We consider these peaks to be β -transitions. From more extensive DMTA measurements of the PMMA-based ionomers with various ion contents, with starting temperature from -100 to -50 °C, it was determined that the β -transitions labeled $T_{\beta 1}$ and $T_{\beta 2}$ were present. These values are also listed in Table 2 and plotted versus ion content in Figure 11. The two peaks are rather broad and close to each other so that some degree of overlap occurs. Due to the difficulty in determining the exact peak temperatures, we put an estimated error bar of ± 10 °C on the values shown in Figure 11.

For both pure PMMA and the 24.7 mol % ionomer, only one secondary transition peak was found. This is consistent with the results obtained for the primary transitions. For pure PMMA, there is no ionic peak as there is no ionic phase. For the 24.7 mol % ionomer, all the polymer chains are expected to be involved in the ionic cluster phase so that there is no ion-poor phase. For ionomers with ion contents of 6.0 and 12.4 mol %, two secondary transitions (designated here as β_1 - and β_2 -transitions) were found for each ionomer, and these are attributed respectively to an ion-poor phase and to an ion-rich phase. It is clearly shown in Figure 11 that the two secondary transition temperatures increase with ion content, as the two primary transition temperatures also did (see Figure 6). Such a result has not been reported to the best of our knowledge. It is reasonable to conclude that the two different environments formed in the ionomers (i.e., an ion-poor phase and an ion-rich phase) have different degrees of restrictions to large-scale (α -transition) and local (β -transition) motions, and this difference is reflected in two relaxation peaks (T_{g1} and T_{g2} for the α -transition and $T_{\beta 1}$ and $T_{\beta 2}$ for the β -transition).

The finding that local molecular motion is also affected by ionic aggregation is important because it provides a means to study the structures and stability of ionic aggregates in ionomers via secondary transitions. The 24.7 mol % ionomer is a good example. It is

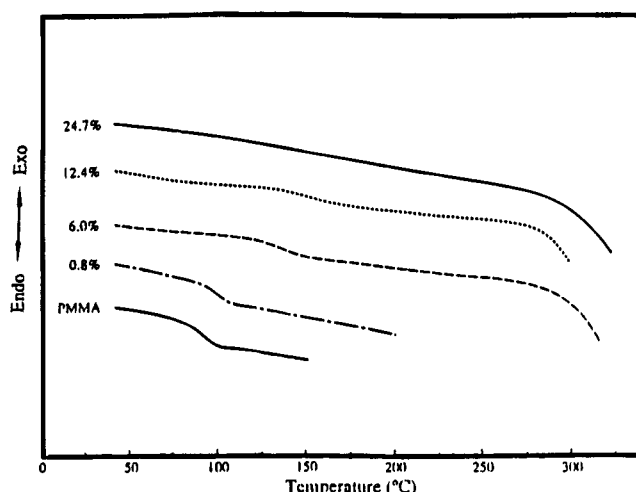


Figure 12. DSC results for PMMA-based sodium ionomers with various ion contents.

difficult to directly observe the primary transition peak of this ionomer as the peak is expected to be at a temperature higher than or overlapped with the decomposition peak. However, at lower temperatures, only one secondary transition peak (i.e., the β_2 peak) is evident, and this is indicative of the disappearance of the ion-poor phase (i.e., the β_1 peak). The position of the secondary transition is also important because it is closely related to low-temperature toughness of polymeric materials.⁵⁶

DSC Results for PMMA Ionomers. Differential scanning calorimetry (DSC) is the most frequently used technique for thermal analysis of polymers.⁵⁷ It measures the difference in energy inputs into a substance and a reference material as they are subjected to a controlled temperature program. All the chemical and physical processes involving enthalpy change or heat capacity change can be investigated with DSC. A glass transition temperature appears as an endothermic incremental step in a heating curve.

Figure 12 is a group of DSC heating curves for PMMA ionomers (sodium salt) with various ion content. It is seen that the glass transition temperature, which corresponds to the matrix T_g by DMTA, shifts to higher temperature as the ion content increases. The DSC data are also listed in Table 2 together with the DMTA data. The glass transition temperatures from DSC are also plotted as a function of ion content in figure 6. T_g increases almost linearly with ion content, at a rate of about 6.5 °C/(mol % ion content), which is close to but slightly higher than that obtained from dynamic mechanical thermal analysis (5.5 °C/(mol % ion content)). Again, the line is drawn according to the least-squares method. All the glass transition temperatures from DSC are consistently lower than those from DMTA (taken as the peak position of $\tan \delta$ curve), which is an expected result as the DMTA data has been obtained at frequency of 1 Hz.⁴⁹

It should be added that some ionomer systems, such as poly(styrene-co-sodium methacrylate) and poly(ethyl acrylate-co-acrylate) ionomers, show two glass transitions by DSC, corresponding to a matrix T_g and a cluster T_g , while some ionomer systems, such as poly(styrene-co-cesium acrylate) and poly(vinylcyclohexane-co-acrylate) ionomers, only show a single glass transition by DSC, corresponding to a matrix T_g .^{23,58,59} Although the reasons for the appearance of only a single T_g are unclear, it is suggested that it may be due to the small

Table 3. Dynamic Mechanical Thermal Analysis Results for Poly(styrene-co-sodium methacrylate) Ionomers

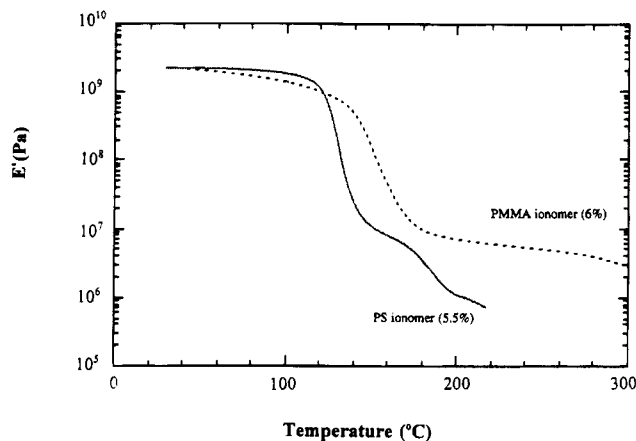
ion content (mol %)	E' (Pa, 30 °C)	T_{g1} (°C)	T_{g2} (°C)	$\tan \delta_1$	$\tan \delta_2$
0.0	1.95×10^9	121		3.42	
5.5	2.18×10^9	132	211	1.27	0.93
8.2	2.39×10^9	142	218	0.57	1.05

heat capacity change for the glass transition of the cluster phase.⁵⁸ The PMMA ionomer seems to be in this category. It is also reported that the glass transitions obtained from DSC and those from E'' peaks are well correlated; for example, T_g s from both methods are in close agreement, and when two E'' peaks are seen, two DSC transitions appear.⁵⁸ For the PMMA ionomers, only a single E'' peak appears as well as a very small shoulder at high temperature (not shown), and DSC shows only the matrix T_g , which also reflects a good correlation between DSC data and E'' data.

Comparison with Poly(styrene-co-sodium methacrylate) Ionomers. Dynamic mechanical properties of PS-based ionomers have been extensively studied. The ionomers investigated were lightly sulfonated PS ionomers^{24–26,45} and poly(styrene-co-metal methacrylate) ionomers.^{5,21–23} To compare our results on the PMMA-based ionomers with those on the PS-based ionomers, we have also examined the dynamic mechanical properties of poly(styrene-co-sodium methacrylate) ionomers using the same equipment, specimens preparation method, and testing conditions as in this work. Since both ionomers have the same ionic units, sodium methacrylate, the effect of the difference in backbone chains may be directly compared. Lightly sulfonated PS ionomers were also studied under the same conditions in this laboratory.²⁴

Since many results on poly(styrene-co-methacrylate) ionomers have already been reported,^{5,21–24,45} we briefly describe major results relevant to the current work on the PMMA ionomers. A plot of storage modulus versus temperature for poly(styrene-co-sodium methacrylate) ionomers indicates a general trend of the DMTA behavior of amorphous ionomers; in the entire temperature range studied, modulus increases with ion content. For ionomers of 5.5 and 8.2 mol % ion content, rubbery plateaus are developed and the increase of the rubbery modulus with ion content is significant. For these ionomers, two peaks are present in a plot of loss tangent versus temperature and both increase with ion content. The low-temperature peak reflects the glass transition of the matrix phase, and the high-temperature peak corresponds to the glass transition of the ionic cluster phase. The 30 °C moduli, the T_g values, and the corresponding loss peak heights for the PS ionomers are summarized in Table 3. The relation between the glassy modulus (30 °C) and the ion content for the PS ionomers is approximately linear as noted also for the PMMA-based ionomers (see Figure 4). In the ion content range studied, the matrix T_g increases with ion content almost linearly. The rate of increase of T_g is around 2.5 °C/(mol % ion content) for the multiplet-containing matrix phase, a value a little lower than that reported recently by Kim et al. (3.3 °C/(mol %)).²³

The peak height values of loss tangent for both the ionic cluster phase and the multiplet-containing matrix phase vary with ion content; the multiplet-containing matrix phase decreases with increasing ion content; while the cluster phase increases with increasing ion content, as noted also for the PMMA ionomers (see Figure 7). The critical ion content at which the cluster

**Figure 13.** Comparison of the storage modulus versus temperature curve for the poly(styrene-co-sodium methacrylate) ionomer (5.5 mol %) with that for the PMMA ionomer (6.0 mol %).

phase begins to dominate over the multiplet-containing matrix phase is found to be ca. 6–7 mol %. This critical ion content is very close to that reported for poly(styrene-co-methacrylate) ionomers (ca. 6 mol %)²² and for partially sulfonated PS ionomers (ca. 6 mol %).²⁴

It is interesting to compare results obtained on the poly(styrene-co-sodium methacrylate) ionomer with those obtained on the PMMA-based ionomers (see Figure 13). The poly(styrene-co-methacrylate) ionomer seems to develop a shorter rubbery plateau than the PMMA-based ionomer. A short rubbery plateau region for the poly(styrene-co-methacrylate) ionomer has been previously reported, and, by comparison with an extended rubbery plateau region of an SPS ionomer,²² it was attributed to the fact that ionic multiplets made of sodium sulfonates are stronger than those made of sodium carboxylates.⁴⁵ However, as seen in Figure 13, an extended rubbery plateau region seems to be found also in the PMMA-based ionomers in which the ionic multiplets are also made of sodium carboxylates. In addition, the cluster T_g s of PMMA ionomers are higher than those of poly(styrene-co-sodium methacrylate) ionomers. Actually, the cluster T_g s of PMMA ionomers are comparable to those of SPS ionomers. For example, at 6 mol %, cluster T_g s (determined as $\tan \delta$ peak positions) are ca. 190 and 240 °C for poly(styrene-co-sodium methacrylate) and SPS ionomers,⁴⁵ and that of the PMMA ionomer obtained in this work is 244 °C. These results indicate that ionic groups, sodium methacrylate, are more stable in PMMA than in PS. The difference between these two ionomers is the type of the base polymer: i.e., PS and PMMA. Both have a quite similar T_g and comparable molecular weight. The differences are dielectric constant and chain flexibility. If the thermal stability of multiplets is the prime factor determining the extent of the rubbery plateau and the value of the cluster T_g , the poly(styrene-co-methacrylate) ionomer should have a more extended rubbery plateau and a higher cluster T_g , because the ionic multiplets in polymers of lower dielectric constant (i.e., PS) are expected to be stronger. However, the results seem to be opposite. We speculate that two possible factors contribute to the longer rubbery plateau and higher cluster T_g for the PMMA ionomers as compared with the poly(styrene-co-sodium methacrylate) ionomers: one is attractive interactions between the ionic groups and the dipoles of the nearby ester groups in the PMMA ionomer. Such interactions may provide a stabilizing

effect on the ionic cross-links that are formed and thereby provide enhanced thermal stability. Another is the possibility that fewer lone ion pairs are present in the PMMA ionomer, since PMMA chains have greater chain mobility than PS chains. This may lead to a greater degree of ionic cross-linking in the PMMA ionomer. Nevertheless, this behavior, as well as the higher rate of increase with ion content of low- T_g peaks for the PMMA ionomers as compared with the PS ionomers, seems to be inconsistent with the new multiplet-cluster model. More work needs to be done to clarify these matters.⁶⁰

Conclusions

PMMA-based ionomers were prepared either by hydrolysis of PMMA or by random copolymerization of component monomers. Their dynamic mechanical properties were studied and discussed in terms of ionomer morphology. It is shown that the modulus of ionomers increases with ion content over the entire temperature range studied: the glassy modulus increases linearly with ion content, while the rubbery modulus increases more dramatically. By comparing rubber elasticity theory with the results obtained on the PMMA-based ionomers and covalently cross-linked PMMA, it is found that, in the low ion content region, both ionically cross-linked and covalently cross-linked PMMA have moduli more or less close to those calculated from the rubber elasticity theory. At high ion content, both ionically cross-linked and covalently cross-linked PMMA show higher rubbery moduli than that predicted by the rubber elasticity theory. However, the ionomers show rubbery moduli significantly higher than those of corresponding covalently cross-linked PMMA at very high ion contents. This indicates the existence of a structure that is more effective in enhancing the rubbery modulus at high ion content; this is believed to be ionic clusters that work as reinforcing fillers. The appearance of a second relaxation peak at higher temperature further confirms the existence of an ion-rich phase for the ionomers with high ion contents. The ion-rich phase increases with ion content, while the ion-poor phase decreases with increasing ion content. For the PMMA-based ionomers, the critical ion content at which the ion-rich phase begins to dominate over the ion-poor phase is around 12 mol %, which is higher than that of PS-based ionomers (ca. 6 mol %). This can be explained by both the classical and the new multiplet-cluster models proposed by Eisenberg.

The glass transition temperatures of both PMMA-based and PS-based ionomers increase with ion content. However, the rate of increase for the PMMA-based ionomers (ca. 6 °C/(mol %)) is higher than that for the PS-based ionomers (ca. 3 °C/(mol %)). This cannot be explained by the multiplet-cluster model. Further investigation is needed to understand this phenomenon.

The nature of the counterion plays an important role in determining the structures and properties of ionomers. A PMMA-based Ca ionomer and a Na ionomer, with the same ion content of 0.8 mol %, have the same glass transition temperature, but the Ca ionomer develops an extended rubbery plateau and a small high-temperature transition peak; this is an indication of the higher strength and stability of the ionic cross-links through ionic aggregation in the divalent Ca ionomers compared with the monovalent Na ionomers.

The effect of ionic interactions on the *secondary transition* of the PMMA-based ionomers was also stud-

ied. We have found that the secondary transition temperature increases with ion content and there appear two secondary transition peaks for the ionomers that also show two primary transition peaks. This is another indication of the existence of two different environments where ionic groups are embedded. Study of secondary transitions may offer a new method to investigate the structure of ionomers. For example, it is difficult to directly observe the primary relaxation peak for the 24.7 mol % ionomer because the peak is expected to be higher than or very close to the decomposition temperature, while the secondary relaxation peak for this ionomer is easily observed.

A systematic study of a new type of amorphous, glassy PMMA-based ionomer is useful not only to test the general applicability of models by comparing their results with those on widely used PS-based ionomers but also to provide new information, such as the effect of ionic interactions on secondary transitions and mechanical properties. The PMMA ionomers may be more useful than the PS ionomers for engineering applications. The results on deformation/fracture behavior of the PMMA ionomers will be reported in the future.

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