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Sizes and Stabilities of Multiplets and Clusters in Carboxylated and Sulfonated Styrene Ionomers

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ABSTRACT: The mechanical properties of some random styrene ionomers are investigated in order to determine the effects of the type of the ionic groups and their position relative to the polymer backbone. Previous studies have shown that increasing the distance of the ion pairs from the polymer backbone leads to larger multiplets and greater intermultiplet spacings in random styrene ionomers. In this study, the position of the ion pairs relative to the polymer backbone is shown to have a profound influence on the mechanical properties of the material. This is attributed to differences in morphology resulting from different extents of steric hindrance to ion-pair aggregation in each ionomer. The strength of the electrostatic interactions between ionic groups is governed by the type of the ionic species. Strong electrostatic interactions between ion pairs tend to give rise to relatively stable multiplets which act as cross-links even at relatively high temperatures. The modulus of the material in the rubbery region remains constant while the multiplets are stable but decreases with the onset of ion hopping. This provides some insight into ion-hopping kinetics.

1. Introduction

Relatively small amounts of ionic groups attached to the chains of an organic polymer of low dielectric constant may exert profound effects on the physical properties of the material. These effects have been attributed to aggregation of the ionic species, although the exact morphologies of the aggregates have not been fully elucidated.[1-14] A wide range of ionomers has been investigated by techniques such as small-angle X-ray[14-16] and neutron scattering;[17] mechanical and dielectric measurements;[18-30] Mössbauer,[31] ESR,[32] IR,[33,34] Raman,[35] and NMR[36] spectroscopy; solution properties;[37,38] and electron microscopy.[39,40] Polystyrene-based ionomers in which the ionic groups are distributed randomly along the polymer chain constitute an important class of ionomers, and a great deal of research has been devoted to the study of their properties. One of the reasons for the interest in these materials is that the absence of crystallinity facilitates studies of the effects of the ion pairs on their physical properties. A number of morphological models have been proposed in order to account for the observations from a wide variety of experimental techniques. These models have been reviewed recently.[10,11,41]

This study brings together a wide range of concepts related to the morphologies and properties of random ionomers. The topics addressed in this study include electrostatic interactions between ion pairs, aggregation of ion pairs, cross-linking effects of the ionic aggregates, filler effects of the aggregates, immobilization of the polymer chains, migration of ion pairs between aggregates, phase separation, and phase inversion.

It is generally accepted that in random ionomers such as poly(styrene-*co*-sodium methacrylate)(PSMa-Na), the ion pairs associate to form quartets, sextets, and aggregates of higher order, collectively known as multiplets.[42] These multiplets act as cross-links and increase the modulus and glass transition temperature (T_g) of the polymer. In a recent model, it has been proposed that each ion pair in a rigid multiplet effectively anchors the polymer chain to which it is attached, thus yielding a region of restricted mobility surrounding each multiplet.[41] If the multiplets are close enough together for these regions of restricted mobility to overlap, larger contiguous regions of restricted mobility are formed. When such a region is large enough to exhibit its own T_g, it behaves as a separate phase and is termed a cluster.

One of the manifestations of phase-separated behavior in these clustered materials is the existence of two peaks in the loss tangent (tan δ) vs temperature curves. The two peaks have been attributed to the glass transitions of the unclustered and clustered regions, respectively.[1-5] The high values of the apparent activation energies of the two transitions indicate that they are both true glass transitions, which implies that the high-temperature dispersion is not necessarily due to complete dissociation of the multiplets into separate ion pairs,[21,26] although it may be related to increased mobility of the ion pairs and release of restricted mobility. This hypothesis is supported by high-temperature SAXS studies which indicate that the multiplets still exist at temperatures above the T_g of the cluster phase.[43-45]

There are several requirements for phase-separated behavior (i.e., clustering) to be observed in ionomers,[41] viz.

(1) The ionic groups must aggregate to form multiplets.

(2) The multiplets must be rigid; i.e., the ionic groups within a multiplet must be firmly anchored and hence reduce the mobility of the polymer chains to which they are attached.

(3) The multiplets must be close enough together to allow some overlap of the region of restricted mobility surrounding each multiplet.

(4) The multiplets must remain in existence above the T_g of the unclustered phase, although some migration of ion pairs between multiplets occurs.

All of these factors are relevant to the present study.

Migration of ion pairs between multiplets is known to occur at elevated temperatures because the ionomers are "melt-processable" despite the fact that multiplets still exist at these temperatures, as evidenced by a small-angle X-ray peak.[14,43-45] The process by which the ion pairs migrate from one multiplet to another has been termed "ion hopping".[46] However, although it is recognized that ion hopping occurs between multiplets at high temperatures, relatively little attention has been focused on this aspect.

Extensive studies on ionomers have demonstrated that a large number of parameters are important in influencing multiplet formation and clustering in random ionomers.

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Among these are the ion content, size of the polyion and counterion, dielectric constant of the host polymer, T_g of the polymer, rigidity or persistence length of the backbone, position of the ion pair relative to the backbone, steric constraints, amount and nature of added plasticizer, thermal history of the sample, etc. Many studies have addressed themselves to the elucidation of these effects.[1-12,41,44,47]

In this study, the properties of random styrene ionomers containing methacrylate, styrene-*p*-carboxylate, and styrene-*p*-sulfonate groups are compared in order to gain some insight into the effects of parameters such as the type and position of the ionic groups on the morphologies and mechanical properties of these materials. The *p*-sulfonated polystyrene ionomers[28-30] and their styrene–methacrylate analogues[19-26] have been studied extensively before. The corresponding *p*-carboxylated styrene ionomers have also been investigated, although to a lesser extent.[14,27,49] Several publications have also compared various aspects of the behavior of these three types of materials.[14,28,48,49] However, a reevaluation of these materials is warranted in light of insights gained from the recently proposed multiplet-cluster model and recent advances in instrumentation.

Sulfonated and carboxylated polyurethane ionomers have also been studied in some detail previously.[50,51] However, the ionic groups are not placed at random intervals along the polymer backbone in these materials and the mechanical properties are complicated by crystallinity. It is thus difficult to make direct comparisons between these materials and the random polystyrene-based ionomers investigated in the present study.

This study addresses factors such as the effects of differences in the relative sizes and stabilities of multiplets and the propensity for phase separation, i.e., cluster formation (as opposed to multiplet formation), in these random styrene ionomers. Previous studies on these materials were carried out in a number of laboratories on different instruments under different conditions. In order to minimize any differences in instrumentation, molecular weight, drying conditions, etc., in this study, samples were prepared and measured under identical conditions. The results for the poly(styrene-*co*-alkali methacrylate) ionomers have been presented in a separate publication.[26]

A comparison of the data for the *p*-carboxylate and *p*-sulfonate ionomers allows the elucidation of the effect of the *type* of the ionic group on the physical properties of the material. Comparison of the properties of the *p*-carboxylated styrene ionomers with those of analogous poly(styrene-*co*-alkali methacrylates) allows the effects of the *position* of the ionic species relative to the polymer backbone to be determined. The poly(styrene-*co*-alkali methacrylate) ionomers are denoted by PSMa-X, the *p*-carboxylated ionomers by PSC-X, and the *p*-sulfonated ionomers by PSS-X, where X represents the alkali-metal counterion.

Previous studies on side-chain ionomers have shown that the size of the multiplets increases with increasing distance of the ionic species from the polymer backbone.[47] This has been attributed to reduced steric hindrance to ion-pair aggregation as the distance from the backbone is increased. In the methacrylate ionomers, the ionic groups are situated much closer to the backbone than in the *p*-carboxylate or *p*-sulfonate ionomers. Steric constraints are thus expected to be significantly more acute in the methacrylate ionomers, resulting in smaller multiplets which are more closely spaced. It is important to note that, at a particular ion content, there is a significantly higher number of multiplets per unit volume of the methacrylate ionomer than the *p*-carboxylate or *p*-sulfonate ionomers.

Provided that the multiplets are rigid, the thickness of the restricted mobility region surrounding each multiplet depends on the persistence length of the host polymer and is independent of the size of the multiplet.[41] Hence, the volume of material with restricted mobility per ion pair decreases as the size of the multiplets increases. Thus a significantly higher volume fraction of the material is expected to be restricted in mobility in the methacrylate ionomers than in analogous ionomers with larger multiplets. Hence, it is anticipated that overlap of these regions and the onset of cluster formation should also occur at lower ion concentrations in the methacrylates and should be reflected in properties such as the magnitudes of the high-temperature loss tangent peaks and the values of the moduli.

Rigid multiplets may be considered to behave as ultrafine particles of a reinforcing filler in the host polymer.[50] For a given filler content, the number of filler particles per unit volume of the material increases with decreasing size of the particles, and the reinforcing effects of the filler tend to be more pronounced. In some filled systems, the polymer chains become chemically bonded to the surface of the filler particles[52] and may thus experience restricted mobility close to the surface of the particle. This is analogous to the restriction in mobility experienced by the ionomer chains attached to an ion pair in a rigid multiplet.

Because the multiplets effectively act as multifunctional cross-links, a rubbery plateau may be observed in the modulus vs temperature curves at temperatures below the cluster T_g, but above the T_g of the unclustered phase, provided that the multiplets remain stable over this temperature range. If the multiplets act as independent multifunctional cross-links, the value of this rubbery modulus is expected to be in keeping with the modulus predicted by the classical theory of rubber elasticity[53]

$$E' = 3\rho RT/M_c \qquad (1)$$

where ρ is the density of the polymer, R is the gas constant, T is the temperature, and M_c is the average molecular weight between cross-links.

However, in addition to acting as cross-links, the multiplets also behave as reinforcing filler particles and may thus further increase the modulus of the system.[50] Hence, if sufficient numbers of the ion pairs are incorporated into multiplets, the observed modulus of the ionomer is expected to be significantly higher than that predicted theoretically. Furthermore, as the ion content is increased, the restricted regions surrounding the multiplets begin to overlap. When this occurs, the multiplets no longer behave as independent multifunctional cross-links but act cooperatively to form large regions of restricted mobility which also increase the modulus of the material in the rubbery region. The difference between the experimental and theoretical moduli will increase as the cluster phase becomes continuous and phase inversion occurs.[26]

Another factor to consider is the stability of the multiplets. A well-defined rubbery plateau in the modulus vs temperature curve for an ionomer is only expected if the ion pairs remain firmly anchored in the multiplets for the duration of the modulus measurement. As the temperature is increased, a point is reached at which migration of ion pairs between multiplets occurs within the timeframe of the measurement, thus giving rise to a decrease in the observed modulus. Determination of the temperature at which ion hopping commences at different frequencies yields considerable insight into the kinetics of the ion-hopping process. By contrast, if the multiplets are not stable above the T_g of the unclustered phase, ion hopping will cause a continuous decrease in the modulus of the material, and no well-defined rubbery plateau will be observed.

This study addresses the effects of factors such as the type of the ionic groups and their position relative to the polymer backbone on the size and thermal stabilities of the multiplets. The sizes and stabilities of the multiplets, the extent of clustering, and phase dominance are related to the mechanical properties of various PSMA-X, PSS-X, and PSC-X ionomers. On the basis of the conclusions of this study, it is postulated that ionomers containing sulfonate groups connected directly to the polymer backbone will exhibit mechanical properties which are significantly different from those materials investigated here.

2. Experimental Section

Polystyrene was prepared by bulk free-radical polymerization using benzoyl peroxide initiator. The weight-average molecular weight was determined by gel permeation chromatography to be ca. 1.20×10^5 with a polydispersity index of ca. 1.9. Samples of this polystyrene were sulfonated in the para position of the styrene ring by treatment with acetyl sulfate in 1,2-dichloroethane at 50 °C. Details of the synthesis procedure are reported elsewhere.[54]

Samples of *p*-carboxylated polystyrene were prepared by first acylating the polystyrene in the para position with acetyl chloride via a Friedel–Crafts reaction using aluminum chloride as a catalyst. The acetyl group was subsequently oxidized with sodium hypochlorite and then acidified to yield the carboxylic acid. The synthesis procedure will be reported in detail in a subsequent publication.[55]

The ion content of each polymer was determined by titration in a 90:10 benzene/methanol solution with methanolic sodium hydroxide using phenolphthalein indicator. Samples of each material were neutralized by the addition of the appropriate amount of a standard hydroxide solution and subsequently freeze-dried. Samples were prepared for mechanical measurements by drying the ionomers in a vacuum oven at ca. 100 °C, followed by compression molding into blocks 36 × 12 × 2 mm at 20 MPa pressure for 10 min at temperatures approximately 20 °C above their glass transition temperatures. The samples were annealed for 24 h under vacuum at temperatures close to their T_g immediately prior to use. Mechanical measurements were performed on a Polymer Laboratories dynamic mechanical thermal analyzer at frequencies ranging from 0.3 to 30 Hz. All measurements were carried out under a nitrogen atmosphere at a heating rate of 0.5 °C/min.

It should be mentioned that, although the samples were prepared under the same conditions, the amount of residual moisture in each sample may vary according to the hygroscopic nature of the ionic groups.

3. Results and Discussion

3.1. Multiplet Stabilities and Ion Hopping. Loss modulus (E'') and loss tangent (tan δ) data, measured at 1 Hz for a sample of *p*-sulfonated polystyrene sodium salt (PSS-Na) containing 6.2 mol % ionic groups, are plotted as a function of temperature in Figure 1. High-temperature peaks resulting from the glass transition of the cluster phase are clearly evident in these curves. However, the height, area, and precise position of the high-temperature tan δ peak are difficult to determine, due to the fact that the baseline is quite steep in this region. Uncertainty in the position and shape of the baseline curve, especially at higher frequencies, precluded accurate determination of the apparent activation energies of the cluster transitions from the loss tangent data.

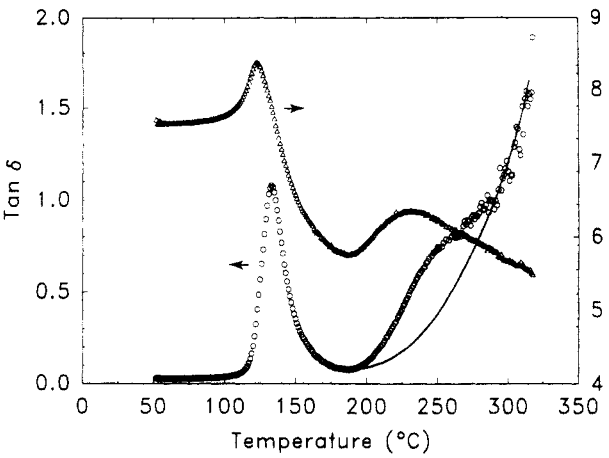

Figure 1. Loss modulus (E'') and loss tangent (tan δ) vs temperature curves measured at 1 Hz for *p*-sulfonated polystyrene sodium salt (PSS-Na), containing 6.2 mol % ions. The solid line indicates a possible base line.

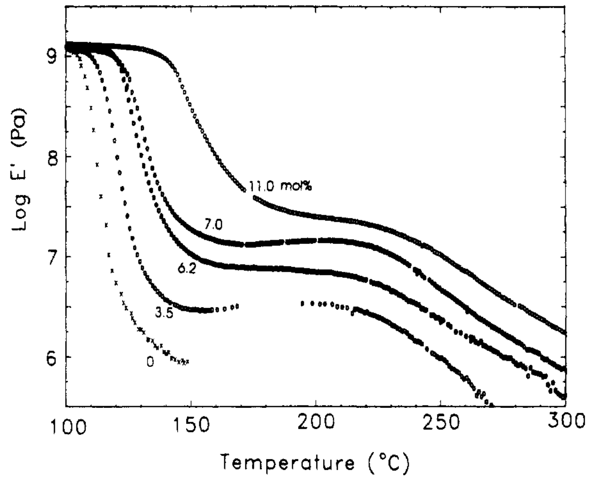

Figure 2. Dynamic storage modulus (E') vs temperature curves measured at 1 Hz for (PSS-Na) ionomers, with a range of ion contents. The molar ion content is indicated for each curve.

Dynamic storage modulus (E') vs temperature curves, measured at 1 Hz for (PSS-Na) ionomers with a range of ion contents, are presented in Figure 2. The molar ion content is indicated for each curve. An extended rubbery plateau is evident in each of these curves and has been shown in a number of studies to occur in modulus vs temperature curves for PSS-Na samples with an ion content greater than ca. 3.5 mol %.[28-30] The plateau in each curve is believed to exist because the multiplets effectively form multifunctional cross-links which remain stable, with little or no migration of ion pairs between multiplets, over the temperature range of the plateau at the frequency of the experiment. As the temperature is raised, a point is reached at which a sufficient number of ion-hopping events occur within the time frame of the experiment, to yield a detectable drop in the modulus by effectively reducing the cross-link density of the material. The temperature above the plateau region at which the modulus begins to decrease depends on the strength with which the ion pairs are held in a multiplet and is relatively insensitive to the ion content. However, the effective cross-link density increases with increasing ion content, resulting in an increase in the glass transition temperature and a higher temperature for the onset of the rubbery plateau region. Because the onset temperature of the rubbery plateau region increases significantly with increasing ion content whereas the upper temperature limit of the plateau region remains fairly constant, the length of the rubbery

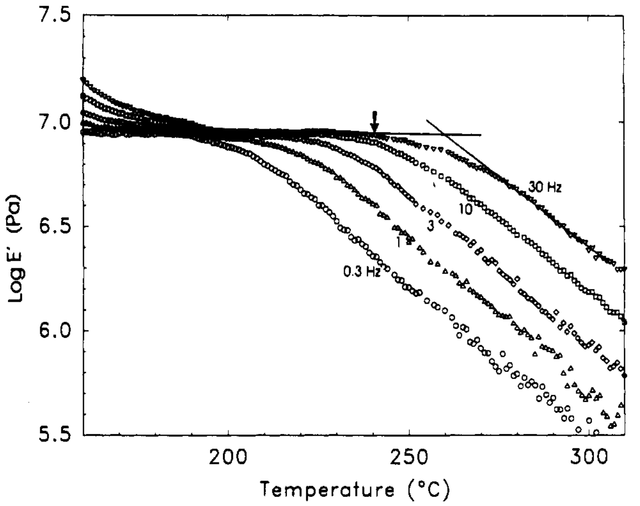

Figure 3. E' vs temperature curves measured at several frequencies for a PSS-Na sample containing 6.2 mol % ionic groups. The frequency is indicated for each curve.

Table I
Ion-Hopping Activation Energies for PSS-Na Ionomers

ion content (mol %)	method 1 E_a (kJ mol^{-1})	method 1 r^2	method 1 σ (kJ mol^{-1})	method 2 E_a (kJ mol^{-1})	method 2 r^2	method 2 σ (kJ mol^{-1})
3.5	170	0.994	8	175	0.999	1
6.2	190	0.995	8	171	0.999	1
7.0				223	0.994	10
8.0	220	0.995	9	195	0.998	5
11.0	185	0.981	15	183	0.995	8

plateau decreases with increasing ion content (see Figure 2).

Modulus data obtained at several frequencies as a function of temperature for a PSS-Na sample containing 6.2 mol % ionic groups are plotted on a graph with expanded temperature and modulus axes in Figure 3. The arrow indicates the temperature at which the first decrease in modulus is observed above the plateau region in the 30-Hz curve. This temperature decreases with decreasing frequency (i.e., increasing time frame) of the experiment, thus providing some information regarding the kinetics of ion hopping in these materials. The activation energy of ion hopping was determined from the slope of an Arrhenius plot of log frequency vs reciprocal temperature. A linear least-squares regression was used to determine the standard deviation of the slope, from which the standard deviation of the activation energy, σ, could be calculated. The activation energies of ion hopping derived in a similar manner for PSS-Na ionomers containing a variety of ion concentrations were found to be in the range 170–225 kJ mol^{-1}, as shown in Table I. However, in the modulus vs temperature curves from which these activation energies are derived, the exact point of the onset of decline in modulus above the plateau region is often difficult to ascertain precisely, leading to considerable uncertainty in the activation energies.

Because the exact point of the onset of the decline in modulus was difficult to determine precisely in all cases, an alternative method (method 2) of determining the activation energies was employed. This entailed linear extrapolation of the rubbery plateau and the high-temperature region of each E' vs temperature curve to yield an intersection point as illustrated for the 30-Hz curve in Figure 3. Intersection points were obtained in this manner for all of the modulus vs temperature curves for the PSS-Na samples. In many cases, the precise intersection point was more readily determined than the exact point of the onset of decline in modulus. The temperatures corresponding to these intersection points were used in the Arrhenius equation to calculate activation energies as described above. The activation energies thus calculated were found to lie in the same range as those derived previously but with better linear least-squares correlation coefficients, r^2, for the Arrhenius fits (see Table I).

In each case, the calculated activation energy was found to have a standard deviation of 15 kJ mol^{-1} or less. Thus, within the confidence limits of the data, no dependence of the activation energy of ion hopping on the ion content of the ionomer could be ascertained.

The curves shown in Figure 3 all have strikingly similar shapes in the region close to the point at which the modulus begins to decrease in each case as described above. It is recognized that these curves could be shifted horizontally to obtain a high degree of overlap of all of the curves at a particular reference temperature. The shift factors thus obtained could be used in a WLF-type equation[56] in a similar fashion to shift factors obtained from stress-relaxation experiments.[20,27,28] However, due to the relatively narrow range of frequencies employed in this study, analysis of the data in terms of the Arrhenius equation is equally appropriate.

It is interesting to note that the activation energies for ion hopping determined in this study for PSS-Na ionomers are considerably higher than the calculated value of the electrostatic energy of attraction between two ion pairs.[57] However, the range of activation energies determined here overlaps with the range of apparent activation energies of the cluster glass transitions determined from the loss tangent peak positions in PSMa-Na ionomers.[26] This suggests a possible interrelation between the ion-hopping process and the high-temperature relaxation in these materials. The cluster glass transition occurs at a temperature at which the segments of the polymer chains with restricted mobility begin cooperative motions consistent with glass transition phenomena within the time frame of the experiment. There are several possible mechanisms consistent with the multiplet-cluster model,[41] by which the clustered material could undergo a glass transition:

(1) If the multiplets are extremely stable at elevated temperatures, it is conceivable that the mobility of the polymer chains in the immediate vicinity of a multiplet may increase to the point where the material with restricted mobility undergoes a glass transition *without* either decomposition of the multiplet or even significant ion hopping.

(2) Another possibility is that the multiplet remains intact with relatively little ion hopping at elevated temperatures, but the rigidity of the multiplet is reduced, thus allowing increased motion of the polymer chains attached to the ion pairs in the multiplet accompanied by a reduction of the thickness or elimination of the restricted mobility layer.

(3) A third mechanism is related to a relatively high rate of ion hopping between multiplets. During an ion-hopping event, the migrating ion pair no longer anchors the polymer chain to which it is attached. Thus the polymer chain segments adjacent to the ion pair experience an increase in mobility during an ion-hopping event. The motions in these chain segments during the ion-hopping period are likely to be consistent with glass transition phenomena. If the rate of ion hopping is high enough, significant numbers of these chain segments may undergo increased motions within the time frame of the experiment. In this case, the mechanisms of ion hopping and of the

high-temperature transition would be interrelated.

If the high-temperature transition occurs by either of the first two mechanisms, the multiplets would still act as multifunctional cross-links and as filler particles above the second T_g. Thus, above the cluster T_g, the modulus of the sample would ultimately reach a relatively constant value based on the effective cross-link density and filler content of the material. Only the contribution to the modulus from the regions of restricted mobility would disappear. Hence, an additional plateau would be anticipated in the modulus vs temperature curves above the cluster T_g. It should be noted that the modulus value for such a plateau would be significantly higher than that expected on the basis of simple entanglements.

However, if ion hopping is involved in the high-temperature relaxation, the rate of ion hopping would be expected to increase with increasing temperature, and the modulus of the material would thus continue to decrease. Modulus vs temperature curves obtained in this study indicate a fairly rapid decrease in modulus above the cluster T_g with no evidence of an additional plateau intermediate between the first rubbery plateau and the entanglement plateau. This indicates that ion hopping is directly involved in the high-temperature relaxation mechanism as described above.

The exact nature of the relationship between ion hopping and the cluster glass transition is not discernible from this study. On the one hand, migration of an ion pair between multiplets may be induced by the increased thermal energy of the ion pair, resulting in increased mobility of the adjacent chain segments. On the other hand, as the temperature of the system is increased, the mobility of the constrained segments is also expected to increase. The motions of these chain segments exert an entropic pull on the ion pairs to which they are attached and may ultimately induce ion hopping between multiplets. In the first instance, increased chain mobility *results from* ion hopping; migration of ion pairs between multiplets would occur even if the polymer chains were not attached to them. In the second instance, increased chain mobility *induces* ion hopping; migration of ion pairs would not occur without the entropic pull of the attached chains.

It should be noted that, in each E' vs temperature curve, the onset of the drop in modulus above the plateau region occurs at considerably lower temperatures than the cluster peaks in the corresponding E'' or tan δ curves. Thus, significant ion hopping already occurs below the T_g of the cluster phase. The secondary relaxations with relatively long relaxation times observed in these materials[28,30] may well be related to the ion-hopping mechanism below the cluster T_g.

If the cluster phase is continuous, the long relaxation times below the cluster T_g result in a breakdown of the time–temperature superposition in stress-relaxation data. The time–temperature superposition does not apply to stress-relaxation data obtained for PSMa-Na ionomers containing more than 6 mol % ions when the stress-relaxation experiments are conducted at temperatures below 180 °C but is reestablished at higher temperatures for the same materials.[19,24] Below the cluster T_g, the clusters constitute a continuous separate phase with relatively long stress-relaxation times. Above the cluster T_g, the entire material consists of a single phase, and thus only a single relaxation time is observed. At temperatures above the cluster T_g, it is not possible to distinguish material which was originally in the clusters from that which was in the unclustered phase below the cluster T_g.

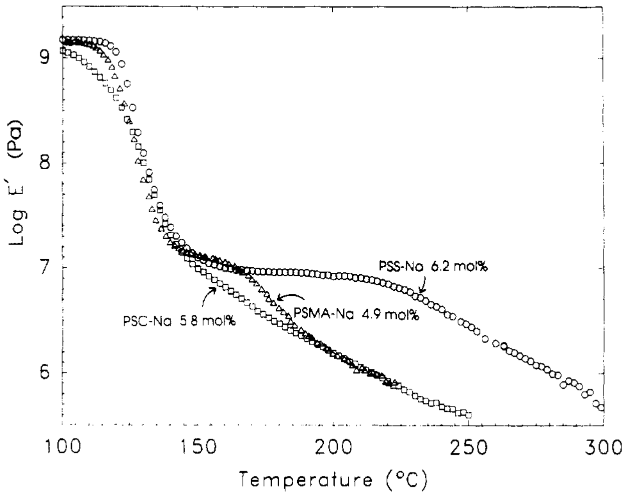

Figure 4. E' vs temperature curves measured at 1 Hz for PSMa-Na, PSS-Na, and PSC-Na samples containing ca. 6 mol % ions.

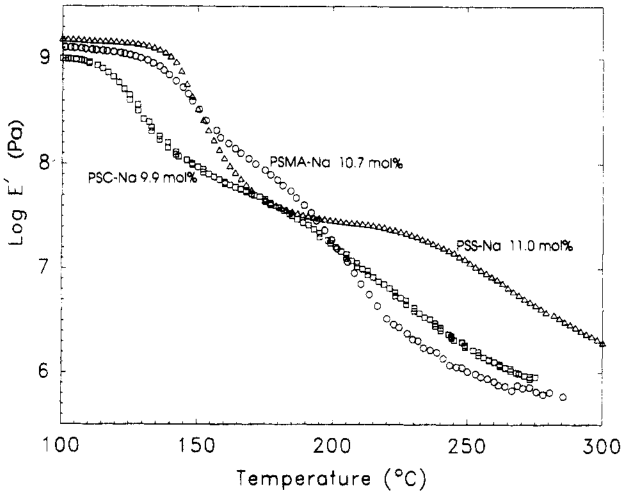

Figure 5. E' vs temperature curves measured at 1 Hz for PSMa-Na, PSS-Na, and PSC-Na samples containing ca. 11 mol % ions.

The interrelation between ion hopping and the glass transition may also account for the breadth of the cluster glass transition. The cluster glass transition is considerably broader than the glass transition of the unclustered phase. This may be due to a gradual increase in the extent of ion hopping with increasing temperature. Ion pairs in isolated multiplets or in multiplets near the surfaces of clusters are expected to migrate more readily than those in multiplets situated well within the clustered regions. As the temperature of the system is increased, the volume of the clusters (i.e., large regions of restricted mobility) will progressively decrease, due to the material at the surface of the clusters undergoing its glass transition earlier than the material at the center of the clusters. This progressive reduction in the volume of the cluster phase with increasing temperature is postulated to give rise to the relatively broad cluster glass transition.

Modulus vs temperature curves measured at 1 Hz for PSMa-Na, PSS-Na, and PSC-Na are shown in Figures 4 and 5 for samples containing ca. 6 mol % and ca. 11 mol % ions, respectively. The molar ion concentration for each material is indicated on the graphs. It is evident that the plateau regions are much more well-defined in the modulus curves obtained for the PSS-Na samples than in those obtained for the corresponding PSMa-Na or PSC-Na materials. This implies that the multiplets in the *p*-sulfonate ionomers are kinetically more stable than those in the analogous *p*-carboxylate or methacrylate ionomers,

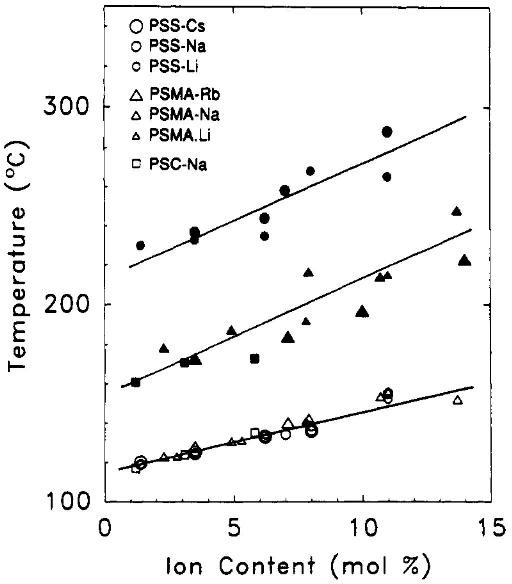

Figure 6. Loss tangent peak positions measured at 1 Hz for a number of random styrene ionomers. Open symbols indicate low T_g phases; filled symbols indicate cluster phases.

as has been recognized before.[28,30,49,50] This is most likely due to stronger electrostatic attractive forces between the sodium sulfonate groups in a multiplet than those between sodium carboxylate groups. Furthermore, the length of the plateau also depends on the counterion, indicating that the strength of the electrostatic interactions is also important in this context.[29]

The positions of the loss tangent peaks associated with the T_g's of the cluster phases in these materials provide further evidence to suggest that the electrostatic attractive forces between ion pairs are stronger in the sulfonated ionomers than in those containing methacrylate or *p*-carboxylate groups. The loss tangent peak positions measured at 1 Hz for a number of ionomers are presented as a function of ion content in Figure 6. It is clear from these data that the T_g of the cluster phase is significantly higher in the sulfonated ionomers than in the corresponding methacrylate or *p*-carboxylate materials. This may be ascribed to stronger electrostatic attractions between sulfonate ion pairs which tend to hinder ion hopping. The loss tangent cluster peaks for the PSS-Cs ionomers occurred at lower temperatures than the cluster peaks for the corresponding PSS-Na or PSS-Li ionomers and are omitted from Figure 6 for clarity.

3.2. Multiplet Size and Spacing. Provided that the aggregation of ion pairs is energetically favorable, one of the most important factors governing the size of the aggregates is the extent to which the ion pairs are sterically hindered. Steric hindrance to ion aggregation is expected to be significantly more acute in the methacrylate ionomers than in the para-functionalized ionomers investigated in this study. Indeed, the Bragg distances derived from the peaks in small-angle X-ray scattering data are ca. 37 Å for PSS-X,[9,58] 31 Å for PSC-X,[59] and ca. 23 Å for PSMa-X[23,47,60] and are relatively insensitive to changes in the type of counterion or the ion content. The Bragg distance is thought to represent the most prevalent spacing between multiplets;[41] thus, the average distance between the multiplets increases with increasing Bragg distance. Assuming that a similar fraction of ion pairs aggregate to form multiplets in each system, the size of the multiplets must also increase with increasing intermultiplet spacing. This implies that the methacrylate ionomers contain small multiplets which are relatively closely spaced, the *p*-sulfonate ionomers contain relatively large multiplets which are comparatively far apart, and that the multiplet sizes and spacing are intermediate in the *p*-carboxylate ionomers. Although the ionic groups in *p*-sulfonate and *p*-carboxylate ionomers have similar steric constraints to aggregation, X-ray scattering experiments indicate that the multiplets are larger and further apart in the *p*-sulfonate ionomers than in the *p*-carboxylate ionomers. This is probably due to stronger electrostatic attractive forces in the *p*-sulfonate ionomers than in the *p*-carboxylate ionomers. It is likely that the stronger forces in the *p*-sulfonate ionomers are able to overcome some of the energy barriers to conformational rearrangement in the system so as to allow more ion pairs to come into direct contact with each other and thus form a relatively large multiplet.

All of the random polystyrene ionomers investigated in this study have similar backbone flexibility and the ion pairs are attached to the backbone by a relatively short, inflexible link. Thus the thickness of the layer of restricted mobility surrounding the multiplets is expected to be similar in each material. If this is the case, then the ratio of the volume of the multiplet core to the volume of the layer of material with restricted mobility surrounding the multiplet decreases with increasing size of the multiplet; i.e., the volume of restricted material per ion pair decreases as the size of the multiplet increases. Hence, the volume fraction of restricted material is lower in materials containing large multiplets than in analogous materials containing smaller multiplets.

For the purposes of an illustrative calculation, all of the ion pairs are assumed to aggregate to form multiplets on a cubic lattice. In a methacrylate ionomer with an intermultiplet distance of 23 Å, each multiplet contains an average of 4.2 ion pairs in an ionomer with an ion content of 6 mol %. In a *p*-sulfonate ionomer with the same ion content but an intermultiplet spacing of 37 Å, each multiplet contains an average of 16.6 ion pairs. If each ion pair occupies a volume of 20 Å^3 and all of the material within 10 Å of the surface of the multiplets is appreciably restricted in mobility, then the volume of immobilized material per ion pair is approximately 2000 Å^3 in the methacrylate ionomer and only ca. 740 Å^3 in the *p*-sulfonate ionomer. If it is further assumed that both materials have the same density, then it can be readily shown that the methacrylate ionomer contains more than 4 times as many multiplets per unit volume as the *p*-sulfonate ionomer.

Thus it is expected that the methacrylate ionomers, which contain small multiplets relatively close together, will contain a higher volume fraction of material which is restricted in mobility, and that the regions of restricted mobility will overlap more readily, than the corresponding *p*-sulfonate ionomers, in which the multiplets are larger and further apart. The greater extent of cluster formation in the methacrylates should result in a higher rubbery modulus than would be expected on the basis of multiplets which act as independent multifunctional cross-links. Furthermore, owing to their relatively small size and large numbers, the reinforcing filler effect of the multiplets in the methacrylate ionomers is expected to be greater than that of the multiplets in the *p*-sulfonate ionomers. The rubbery modulus of the methacrylate ionomers is expected to be further increased at high ion contents due to phase inversion. In a phase-inverted system, the continuous cluster phase is below its T_g at the inflection point in the modulus curve and has a major influence on the overall modulus of the material. Hence, in terms of the proposed model, it is expected that the rubbery moduli of the *p*-sulfonate ionomers should be closer to the values

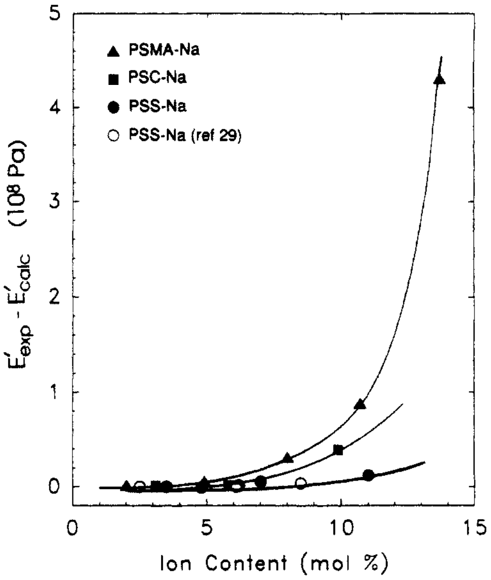

Figure 7. Difference between the measured rubbery moduli and the calculated moduli for PSMa-Na, PSS-Na, and PSC-Na ionomers.

predicted by the classical theory of rubber elasticity than the rubbery moduli of the corresponding methacrylate ionomers. The average multiplet size and spacing in the *p*-carboxylate ionomers are intermediate between those in the methacrylate and *p*-sulfonate ionomers. Thus, it is anticipated that the rubbery moduli of the *p*-carboxylate ionomers should be intermediate between those of the methacrylate and *p*-sulfonate ionomers.

Figure 7 illustrates the deviation of the measured moduli from the calculated values for the materials investigated in this study. The modulus values for the methacrylate ionomers are significantly higher than the calculated moduli, especially at high ion contents. In terms of the multiplet-cluster model, this behavior is in keeping with a material which contains a large number of small multiplets per unit volume and indicates that considerable cluster formation occurs at relatively low ion contents in these materials. At high ion contents, the large difference between the experimental and theoretical moduli may be accounted for by a continuous cluster phase and probably complete phase inversion. In contrast to the methacrylates, the modulus values of the plateau regions in the modulus vs temperature curves for the *p*-sulfonated ionomers are much closer to the values calculated from the theory of rubber elasticity. This indicates that, in these materials, the multiplets tend to act as individual cross-link centers with relatively little cluster formation. The reinforcing filler effect of the multiplets is also not very pronounced in these ionomers. This is in keeping with the properties expected for ionomers containing relatively few, large multiplets per unit volume. Although only a few data for the *p*-carboxylate ionomers are presented in Figure 7, they are in qualitative agreement with a material containing multiplets intermediate in size and spacing between the methacrylate and *p*-sulfonate ionomers.

The rubbery moduli of some of the *p*-sulfonate ionomers were found to be *lower* than the moduli predicted by the theory of rubber elasticity, in agreement with previous studies.[29] This is possibly due to a significant number of lone ion pairs which may not aggregate to form multiplets. It is highly likely that the corresponding *p*-carboxylate and methacrylate ionomers contain at least as many lone ion pairs due to the weaker electrostatic attractions between carboxylate groups than sulfonate groups. However, the multiplets which do form in the methacrylate and *p*-carboxylate ionomers have a greater effect on the modulus than those in the sulfonate ionomers. Thus the moduli of these materials are greater than the calculated values despite the fact that significant numbers of the ion pairs do not aggregate. It should be noted that, at sufficiently high ion contents, the *p*-carboxylated and *p*-sulfonated ionomers do exhibit evidence of a separate cluster phase, but the extent of clustering is evidently lower than in the corresponding methacrylate ionomers.

Rubbery modulus values higher than those expected on the basis of simple cross-linking may be due to a reduction in the effective molecular weight between cross-links, M_c, and/or to phase inversion. Some of the repeat units adjacent to the multiplets are restricted in mobility and thus do not contribute to the effective M_c in the rubbery region. The repeat units with restricted mobility may be in the cluster phase, or they may be close to the surface of an isolated multiplet in the unclustered region. At high ion contents, the cluster phase is believed to comprise the bulk continuous phase, and the material is said to be phase-inverted.[26] In such a case, the modulus of the cluster phase has a very pronounced effect on the mechanical properties of the material and large differences between the measured and calculated moduli are expected.

No abrupt change in the relative volume fractions of the clustered and unclustered phases is expected with increasing ion content. Thus the onset of continuity of the clusters and phase inversion does not necessarily lead to an abrupt change in all of the physical properties of the material. No discontinuities are observed in the position of the loss tangent peak associated with the cluster phase throughout the range of ion contents studied (see Figure 6). For the methacrylate ionomers, the modulus values at the inflection point in the stress-relaxation master curves exhibit no abrupt change with increasing ion content.[20] Similarly, the point at which percolation paths are first formed in the cluster phase, i.e., phase continuity is established, is not expected to coincide with an abrupt change in the viscoelastic properties of the material. However, other features, such as the breakdown of the time–temperature superposition, are consistent with a significant change in morphology over a narrow range of ion contents.

It is very noteworthy that, in a completely independent study of heat capacities based on DSC measurements of sulfonated polystyrene ionomers, Risen and co-workers also concluded that some of the repeat units adjacent to the sulfonate groups are constrained in motion and thus do not participate in the low-temperature glass transition.[61] This finding is in excellent agreement with the proposed multiplet-cluster model[41] and is in keeping with the concept that multiplets act as reinforcing filler particles.

3.3. Decomposition. The mechanical data obtained for the PSS-Na ionomers of higher ion content exhibit a sharp discontinuity at ca. 320 °C which is independent of the frequency of the experiment. Behavior of this type is in keeping with a first-order transition. However, thermogravimetric analysis indicates that significant weight loss of the sample occurs at this temperature, indicating that the features observed in the mechanical data at 320 °C are probably due to desulfonation or other thermal degradation of the sample.

3.4. Predictions. This study elucidates the effects of the type and position of the ionic groups on the mechanical properties of random styrene ionomers. On the basis of these results, it is possible to make some predictions concerning the mechanical properties of other random styrene ionomers which have not yet been synthesized. One such material is an ionomer containing sodium sulfonate groups attached directly to a polystyrene backbone, as may be envisaged in a copolymer of styrene and (methylvinyl)sulfonic acid sodium salt. The ionic groups in this material would be in the same *position* as those in the analogous PSMa-X ionomer but would be of the same *type* as those in the corresponding PSS-X ionomers. The position of the ion pairs would result in considerable steric hindrance to ion-pair aggregation, resulting in relatively small closely spaced multiplets, similar to the multiplet size and spacing in the analogous methacrylate ionomers. This would result in a high volume fraction of material restricted in mobility and a high degree of clustering due to overlap of the restricted mobility regions in close proximity with one another. In this respect, the material would be similar to the corresponding methacrylate ionomers, with phase inversion occurring at a relatively low ion content. Thus the rubbery modulus of the material would be expected to be significantly higher than that predicted by the theory of rubber elasticity, especially at ion contents greater than 6 mol %. However, in contrast to the methacrylate ionomers, the multiplets would be expected to be stable in the rubbery region due to stronger electrostatic interactions between the sulfonate groups. Thus, a well-defined plateau would be anticipated in the modulus vs temperature curves for these ionomers, similar to the plateaux observed for the PSS ionomers.

Hence, it is postulated that the modulus vs temperature curves for these materials should exhibit extended rubbery plateaux similar to those observed for the *p*-sulfonate ionomers, but at significantly higher modulus values. It should be noted that the chemical stability of such a material is unknown and that the mechanical properties postulated here are based on the assumption that thermal degradation will not occur at temperatures below the cluster T_g. It should also be mentioned that these materials have not yet been synthesized.

4. Conclusions

In this study the effects of the *type* of the ionic groups and their *position* on the mechanical properties of some random polystyrene-based ionomers were investigated. A comparison of the mechanical properties of the *p*-sulfonated and the corresponding *p*-carboxylated polystyrene ionomers illustrates the effects of the *type* of the ionic group. A comparison of the mechanical properties of analogous random styrene ionomers containing methacrylate and *p*-carboxylate groups illustrates the effects of the *position* of the ionic group. The *type* of the ionic species determines the strength of the electrostatic interactions between ion pairs and thus the stabilities of the multiplets. The *position* of the ionic groups determines the extent of steric hindrance to aggregation of the ion pairs and thus the sizes of the multiplets.

4.1. Type of Ionic Groups. The existence of well-defined plateaux in the *p*-sulfonate modulus curves, and the absence of plateaux in the *p*-carboxylate curves, implies that the multiplets in the sulfonated ionomers are more stable at elevated temperatures than the multiplets in the analogous carboxylated ionomers. This phenomenon is attributed to greater electrostatic attraction between sulfonate ion pairs than carboxylate ion pairs. The fact that the cluster T_g is higher for the sulfonated ionomers than the carboxylated materials provides additional evidence for stronger attractive forces between sulfonate ion pairs.

The existence of well-defined rubbery plateaux in the modulus vs temperature curves for the *p*-sulfonate ionomers is attributed to the fact that the multiplets remain stable with little or no migration of ion pairs between multiplets over the temperature range of the plateau at the frequency of the experiment. As the temperature is raised, a point is reached at which a significant number of ion-hopping events occur within the time frame of the experiment. This effectively reduces the cross-link density of the material, resulting in a detectable drop in the modulus. The temperature above the plateau region at which the modulus begins to decrease increases with increasing frequency of measurement, thus providing some information regarding the kinetics of ion hopping in these materials.

4.2. Position of Ionic Groups. No well-defined rubbery plateaux are observed in the modulus vs temperature curves obtained for the methacrylate ionomers or the corresponding *p*-carboxylated polystyrene ionomers. However, the modulus values at the inflection point between the T_g's of the unclustered and clustered phases are significantly higher for the methacrylate ionomers than for the corresponding *p*-carboxylate ionomers. The modulus values at the inflection points for the *p*-carboxylate ionomers are in reasonable agreement with the values calculated from classical rubber elasticity theory. This implies that the multiplets are primarily acting as independent multifunctional cross-links and that there is relatively little cluster formation in these materials. In contrast, the modulus values at the inflection points for the methacrylate ionomers are considerably higher than the theoretical values, suggesting that there is a high volume fraction of clustered material in the methacrylate ionomers. This is attributed to the fact that the multiplets in the methacrylate ionomers are smaller and more closely spaced than those in the corresponding *p*-carboxylate ionomers due to higher steric impedance to ion-pair aggregation in the methacrylates. Because the thickness of the restricted region surrounding each multiplet is independent of the size and spatial distribution of the multiplets, the smaller and more closely spaced multiplets give rise to increased overlap of restricted mobility regions, and hence increased clustering.

Differences between the mechanical properties of the *p*-sulfonate and methacrylate ionomers are due to differences in both the type and position of the ionic groups. In comparing these materials, it should be noted that the ion pairs in the *p*-sulfonate ionomers have lower steric hindrance to aggregation and thus form larger multiplets with greater intermultiplet spacing than those in the analogous methacrylate ionomers. This is reflected in the fact that the moduli in the plateau regions are in reasonable agreement with those calculated theoretically, indicating a relatively low extent of cluster formation.

4.3. Predictions. On the basis of the findings of this study, some of the mechanical properties of an ionomer containing sulfonate groups attached directly to the backbone, poly(styrene-*co*-methylvinyl sulfonate), i.e., the sulfonate analogue of the styrene–methacrylate ionomers, are postulated. In such a material, the ion pairs are expected to experience steric constraints to aggregation similar to those in the analogous methacrylate ionomers due to their position, thus resulting in small, closely-spaced multiplets and hence a high degree of clustering. However, in contrast to the methacrylate ionomers, the increased strength of ion-pair interactions is expected to yield multiplets that would be stable far above the T_g of the unclustered phase. Such an ionomer is therefore predicted to exhibit mechanical properties consistent with extensive cluster formation, and also with stable multiplets. The modulus vs temperature curves for this material are thus expected to exhibit well-defined plateaux over comparable temperature ranges to the *p*-sulfonated styrene ionomers but with modulus values in the plateau regions similar to those observed in the styrene–methacrylate ionomers.

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