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A New Multiplet-Cluster Model for the Morphology of Random Ionomers

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ABSTRACT: A new morphological model for random ionomers is proposed which incorporates the findings of recent dynamic mechanical and X-ray scattering studies. The model is based on the existence of multiplets, which reduce the mobility of the polymer chains in their vicinity. The thickness of the restricted mobility layer surrounding each multiplet is postulated to be of the order of the persistance length of the polymer. Isolated multiplets act as large cross-links, thus increasing the glass transition temperature of the material. As the ion content is increased, the regions of restricted mobility surrounding each multiplet overlap to form larger contiguous regions of restricted mobility. When these regions become sufficiently large, they exhibit phase-separated behavior and are termed clusters. The model is in good agreement with a very wide range of experimentally observed phenomena, especially those based on dynamic mechanical and X-ray scattering techniques.

1. Introduction

Over the past two decades, a considerable amount of research has been devoted to random ionomers due to their unique physical properties.[1-13] A number of models for the morphology of random ionomers have been proposed, none of which are completely consistent with all of the experimental observations on these materials. These models have been reviewed recently.[10,11] It is now generally accepted that the ion pairs aggregate to form quadruplets, sextuplets, and higher aggregates, collectively called multiplets.[14] In addition, ion-rich regions termed clusters may also exist at sufficiently high ion contents in some systems.[14] The clusters behave as a separate phase in that they exhibit their own glass transition temperature (T_g). However, the exact structures of the multiplets and clusters have not yet been fully elucidated. In this paper, a new multiplet-cluster model is proposed, which is based on restricted mobility of the polymer chains in the vicinity of the multiplets and which reconciles some of the apparent inconsistencies in our current understanding of these systems.

The first qualitative model for the morphologies of random ionomers was developed by Bonotto and Bonner in 1968.[15] In the same year, Longworth and Vaughan[16] proposed a model based on the analysis of small-angle X-ray scattering (SAXS) data for poly(ethylene-*co*-methacrylic acid) and its alkali-metal ionomer derivatives. A peak corresponding to a Bragg spacing of ca. 50 Å was observed in the scattering profiles. This "ionic" peak was interpreted as being due to scattering from ordered hydrocarbon chains *between* ionic aggregates rather than the aggregates themselves. This model was shown to have several shortcomings, among which are its inability to account for the fact that cesium salts show a much more intense SAXS peak than lithium salts, as well as the observation that both the melting point and the degree of crystallinity are approximately the same in the acid copolymers and the corresponding salt forms.

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In a theoretical model presented by Eisenberg in 1970,[14] steric effects were postulated to limit the number of ion pairs that can aggregate in a spherical "droplet" without the presence of any intervening hydrocarbon. These small aggregates containing only ionic material and possessing low mass and strong electrostatic interactions were collectively termed multiplets. Electrostatic interactions between multiplets were proposed to favor their agglomeration to form phase-separated regions termed clusters, with elastic forces opposing cluster formation. From theoretical evaluation of the electrostatic and elastic forces in random ionomers of low dielectric constant, cluster formation was inferred to be energetically favorable above a certain critical ion concentration. This model was not based on a detailed analysis of X-ray scattering studies of morphology but was able to account qualitatively for the mechanical data suggesting two phases.

Recent, more sophisticated theoretical approaches by Forsman,[17,18] Dreyfus,[19] and Dayte and Taylor,[20] based on the same principles of electrostatic vs elastic forces due to local chain extension on aggregation of the ion pairs, arrived at similar conclusions to those of the Eisenberg model but provided considerable additional insight. In addition, following the experiments by Earnest et al.,[21] Forsman suggested that the entire polymer coil may expand somewhat on aggregation of the ions.[17,18] However, Squires et al.[22] have suggested that no theoretical justification for overall chain extension is necessary to describe ionic aggregation in ionomers with a random distribution of aggregates.

Marx et al.[23] proposed a model in 1973 in which the "ionic" SAXS peak was ascribed to the electron density difference between the metal cations and the hydrocarbon, with the scattering moieties being treated as points on a paracrystalline lattice. In this model, the size of the aggregates is postulated to be very small in all cases, amounting to no more than septimers, even at relatively high ion contents. Hence, only multiplets are postulated to exist without the occurrence of any clustering or phase separation. The model describes the SAXS peak quantitatively but cannot account satisfactorily for mechanical measurements, which indicate a two-phase morphology in these materials.

A similar model was put forwward by Binsbergen and Kroon in 1973[24] in which the scattering moieties are assumed to be points at the centers of spheres, which are randomly packed. This model has quite similar features to those of the paracrystalline lattice model and likewise does not predict two-phase behavior.

In 1983, Yarusso and Cooper[25] proposed a modified hard-sphere model in which the multiplets are proposed to have liquidlike order and to have a distance of closest approach determined by the layer of hydrocarbon chains attached to and surrounding each multiplet. This model is in excellent agreement with the experimentally determined "ionic" peak in the SAXS profiles of SPS ionomers but makes no attempt to account for the mechanical properties of these materials.

A recent model by Ding et al.[26] based on anomalous SAXS from SPS ionomers accurately describes the entire SAXS profile, including the characteristic upturn in scattering intensity near zero angle. This model also attributes the SAXS ionomer peak to interparticle scattering of hard spheres with liquidlike order but includes the effects of a nonrandom distribution of lone ion pairs, thereby accounting for the small-angle upturn. Again, mechanical effects are not considered.

MacKnight et al.[27] proposed a model in 1974 derived from the radial distribution function of the scattered X-rays for partially neutralized poly(ethylene-*co*-cesium methacrylate) ionomers. This model, known as the "core–shell" model, postulates the existence of clusters with a radius of 8–10 Å, each containing ca. 50 ion pairs. The cluster is shielded from surrounding matrix ions by a shell of hydrocarbon chains that is of the order of 20-Å thick. Electrostatic attraction thus results in a preferred distance between the cluster and matrix ions, i.e. the thickness of the hydrocarbon shell. This preferred distance is assumed to be the origin of the SAXS peak corresponding to ca. 20 Å. It is important to note that the ionic peak is *not* considered to arise from interference *between* scattering centers but rather from *intra*particle scattering. The considerable number of ions per aggregate and the relatively large dimensions of the clusters postulated in this model may provide an explanation for the observed high-temperature T_g.

In 1980 Roche et al.[28] suggested a model that is conceptually similar to the core–shell model but differs in the proposed geometry of the clusters. In this model, the central ionic core is proposed to be lamellar instead of spherical with a region depleted of ions on either side of the lamellar core. This depleted region defines the distance of closest approach of other ion pairs, which constitute the shell. In this model, the spacing between the core and shell accounts for the SAXS peak, and the size of the clusters may be sufficient to explain the observed two-phase behavior.

A number of other treatments have been advanced to describe specific ionomer systems. These include block ionomers,[29] sequential ionomers such as polyurethane-based materials,[30,31] semicrystalline ionomers such as Surlyn,[16] and hydrated systems such as the perfluorosulfonates, e.g., Nafion.[17] As these treatments do not address themselves to dry, noncrystalline random ionomers, they will not be discussed here except for one that is of particular interest to the current system and was developed for halato telechelics by Williams et al.[38,39] Extensive studies on these materials have clearly indicated that they contain only large multiplets.

Two recent experimental results have cast considerable doubt on the models proposed to date for random ionomers. Detailed mechanical studies on poly(styrene-*co*-alkali methacrylate) ionomers indicate that the clusters become dominant and perhaps even continuous at an ion content of ca. 6 mol %.[40] These studies were based primarily on analysis of the loss tangent data (tan δ), which indicate that, for this system, the area under each tan δ peak is representative of the volume fraction of the phase responsible for that peak. Comparison of the relative areas of the loss tangent peaks leads to the conclusion that the volume fraction of the clusters is ca. 50% at an ion content of 6 mol %. This conclusion is reinforced by the storage modulus data as well as by other abrupt changes in properties at approximately the same ion content, such as the breakdown of the time–temperature superposition.

Another recent study suggests that the SAXS peak in random ionomers is due to *inter*particle interference.[41] This study was based on SAXS data for styrene-based ionomers in which the ions were situated at the ends of flexible side chains of varying length. These materials show a linear dependence of the Bragg spacing, d_{Bragg}, on the side-chain length, from very long side chains down to the point where the ionic group is attached directly to the polymer backbone or styrene ring. Since the morphology of the long side-chain ionomers is very likely to be the same as that of the halato telechelics, this implies that morphological continuity extends from the telechelics to random ionomers such as the poly(styrene-*co*-alkali methacrylates). Extensive studies on halato telechelics have indicated that only multiplets exist in these materials and that the SAXS peak is thus due to *inter*particle scattering.[38,39] Hence, it is considered highly probable that the SAXS peak in random ionomers is also due to *inter*particle scattering and thus represents the distance between centers of the scattering moieties.

In order to observe a second T_g, domains must be present that have minimum dimensions of 50–100 Å depending on the technique used to detect the T_g. This estimate was made on the basis of several experimental results. On the one hand, many nonionic copolymers, even those with considerable blockiness, show only a single T_g. On the other hand, block copolymers of styrene and dimethylsiloxane (PDMS), with PDMS block lengths of 1000 units, exhibit two-phase behavior.[42]

The observed d_{Bragg} for dry, noncrystalline random ionomers is generally considerably less than 50 Å, despite the fact that these materials exhibit two tan δ peaks.[25] This raises an apparent inconsistency in models that attribute the SAXS peak to *inter*particle interference, in that the *inter*particle center-to-center scattering distances are smaller than the minimum dimensions of the clusters themselves. Thus, if the "ionic" peak in the SAXS profiles of random ionomers is interpreted as being due to *inter*multiplet scattering, the small size of the multiplets does not allow for explanation of the observed second T_g in dynamic mechanical measurements. On the other hand, while models that ascribe the "ionic" SAXS peak to *intra*particle scattering may account for the second T_g, they do not account for the proposed continuity of morphology between halato telechelics and random ionomers, as demonstrated by the linear dependence of d_{Bragg} on the side-chain length in random side-chain systems.[41]

In this paper, we propose a new model of clustering in random ionomers. This new approach successfully accounts for the observed "ionic" peak in the SAXS data, the high volume fraction and dominance of the clusters at relatively low ion contents, and the continuity of morphology of these materials with that of telechelics. The model is also in keeping with a wide range of other experimental observations, as will be discussed in section 3.

2. The Model

In this section, the parameters that govern the formation and characteristics of multiplets will be discussed; this will be followed by a description of clusters and their properties.

2.1. Multiplets. The formation of multiplets is a crucial element in the current model. The term "multiplet" has exactly the same meaning as in the original theoretical model by Eisenberg,[14] i.e., an aggregate consisting of several ion pairs and containing only ionic material. A number of factors govern the formation of multiplets in random ionomers, some of which are determined by the ionic species themselves and others by the nature of the host polymer.

The most important ionic parameter that affects multiplet formation is the strength of the electrostatic interactions between the ion pairs. This is determined by the sizes of the ions and the partial covalent character of the ionic bond. Although none of these parameters can be varied independently of the others, they are important factors in multiplet formation. If the electrostatic interactions between ion pairs are too weak to overcome the elastic forces of the chains to which they are attached, no multiplets will form. The firmness with which the ion pairs are held together is also determined by the strength of these electrostatic interactions; small highly polar ion pairs interact more strongly and thus tend to be more firmly held than larger groups. The firmness with which the ion pairs are held in a multiplet is an important consideration in the current model, as will be discussed below.

The ion content of the ionomer is also a crucial factor in influencing multiplet formation. The proximity of the ion pairs to one another is determined by the ion content of the system. If the ion pairs are very dilute, they are too far apart to experience significant electrostatic attractions and hence do not tend to aggregate.

The characteristics of the host polymer are also important in determining the extent of multiplet formation in a random ionomer. Low dielectric constant and low T_g of the host polymer tend to favor ionic aggregation, while high dielectric constant and/or high T_g tend to inhibit multiplet formation. The presence of plasticizers, as well as specific interactions between plasticizer or backbone and the ionic groups, also influences the process.[43–46]

In ionomers in which ionic aggregation is energetically favorable, the size of the aggregates is limited by steric factors, barring unusual aggregate geometries. In typical random polystyrene-based ionomers such as the poly(styrene-*co*-alkali methacrylates), steric factors prevent more than a small number of ion pairs from coming into direct contact with one another. The multiplets are thus postulated to be relatively small and rigid in these ionomers.[14] In halato telechelics or ionomers in which the ions are situated at the ends of long flexible side chains, there is less steric hindrance to aggregation and larger multiplets result.[38,39]

Each ion pair in a multiplet effectively anchors the polymer chain at the point to which it is attached. Hence, the mobility of the polymer chain in the immediate vicinity of a multiplet is expected to be greatly reduced relative to that of a chain in the bulk polymer, with the mobility increasing gradually with increasing distance from the multiplet. The firmness with which the ion pair is anchored is important in determining how effectively the mobility of the polymer chain is restricted. Rigid multiplets restrict the mobility of the chains more than multiplets in which the ions pairs can move relative to one another. For rigid multiplets to exist, strong electrostatic interactions must be operative between the ion pairs in the multiplet.

Depending on the number of ion pairs per multiplet, considerable local or short-range chain extension of some of the chains is likely to occur on multiplet formation.[17,18] The locally extended chain segments have fewer available configurations and are thus less mobile than unextended chains. Hence, this extension is believed to enhance the restriction in mobility experienced by the chains in close proximity to their point of attachment to a multiplet.

The chains that are anchored to the multiplet are expected to have an effect opposite to that of a plasticizer by effectively reducing the mobility of neighboring nonanchored chains in the immediate vicinity of the multiplet surface. Each multiplet is therefore surrounded by a region of restricted chain mobility or "skin", as depicted in Figure 1. There is no definite boundary between the region of restricted mobility and the rest of the polymer.

The "skin" surrounding each multiplet is expected to be depleted of ions, since ion pairs very close to a mul-

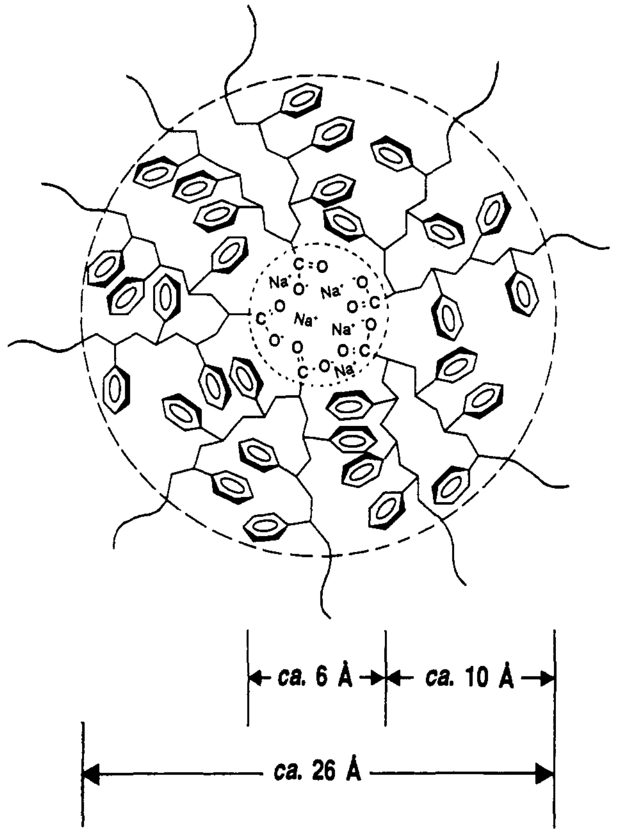

Figure 1. Schematic diagram of the region of restricted mobility surrounding a multiplet in a poly(styrene-*co*-sodium methacrylate) ionomer.

tiplet would experience relatively strong electrostatic forces during multiplet formation and would thus tend to be incorporated into the multiplet itself. Furthermore, two ion pairs very close together on the same chain would also have a very high probability of being incorporated into the same multiplet, with the intervening chain segment effectively forming a short loop emanating from the surface of the multiplet. However, the presence of some lone ion pairs within the region of restricted mobility is not excluded.

The thickness of the region of restricted mobility surrounding each multiplet is determined largely by the flexibility of the polymer backbone; the more flexible the chain, the thinner the "skin" of restricted mobility. The distance over which polymer segments experience an appreciable restriction in mobility is difficult to ascertain exactly but may be assumed to be of the order of the *persistence length* of the bulk polymer. The persistence length is a measure of the distance over which local inflexibility in a polymer chain persists[47] and has been shown to be relatively insensitive to changes in temperature.[48]

A multiplet consisting of only two or three ion pairs will have a relatively lower mass and will therefore be relatively more mobile than a larger multiplet. The number of anchored chains is also lower for small multiplets, resulting in a lower volume fraction of material with reduced mobility in a sphere of radius equal to the persistence length surrounding the multiplet. Conversely, the larger the multiplet, the greater the number of anchored chains and the greater the reduction in mobility. A multiplet containing only two ion pairs, i.e., a quartet, is expected to behave in a similar manner to a conventional cross-link and hence influences the properties of the material in a similar fashion.

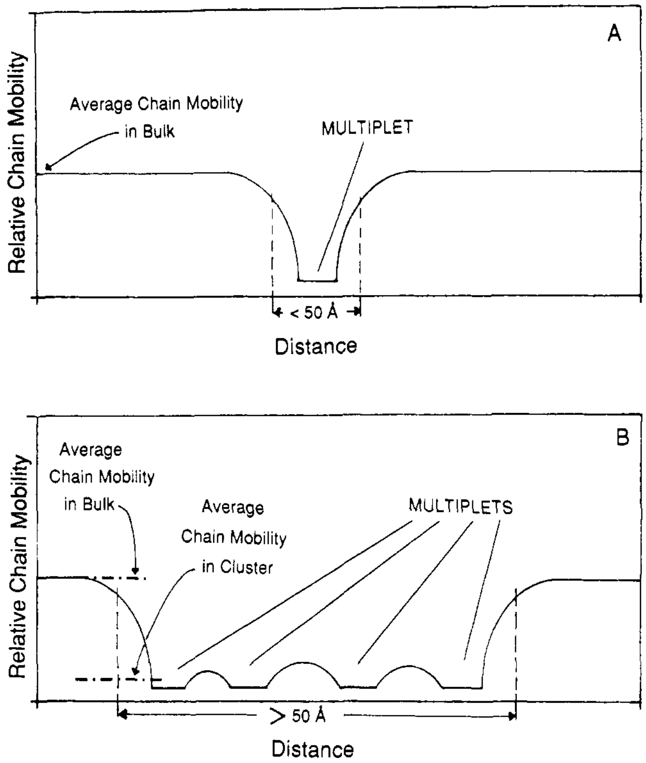

Figure 2. Schematic representation of chain mobility: (A) in the vicinity of an isolated multiplet; (B) in the region of clustered multiplets.

In general, the restricted mobility region surrounding an isolated multiplet would be too small to have its own T_g, but the multiplet itself would increase the T_g of the polymer by acting as a large cross-link.

2.2. Clusters. As the ion content is increased, the average distance between multiplets decreases. Eventually a point is reached where some overlap is encountered among the regions of restricted mobility surrounding each multiplet. It should be stressed, however, that only the regions of restricted mobility overlap; the multiplets themselves remain intact. As this overlap becomes more frequent, relatively large contiguous regions of restricted mobility must form. When such a region is large enough to have its own T_g, it constitutes a cluster and exhibits behavior characteristic of a phase-separated region. It is important to note that, within the framework of this model, cluster formation does not simply lead to broadening of the T_g of the material but gives rise to a new T_g. This is illustrated qualitatively in Figure 2, which schematically compares chain mobility in the vicinity of an isolated multiplet with that in the region of clustered multiplets. Small regions of restricted mobility effectively act as cross-links and thus raise the T_g of the material (Figure 2A). However, when a sufficient number of multiplets are close enough together to form a contiguous region of restricted mobility greater than 50–100 Å in dimension (Figure 2B), the region constitutes a cluster and exhibits its own *separate* T_g.

The exact size of the domains at which two-phase behavior becomes detectable is not well-defined, as is the case in any microphase-separated system. The distance between adjacent multiplets within a cluster must be less than twice the thickness of the restricted mobility layer. No boundaries between overlapping regions within the cluster are proposed to exist.

An important feature of this model is that it does not require the clusters to be of any particular geometry; in fact highly irregular shapes are probable, as depicted in

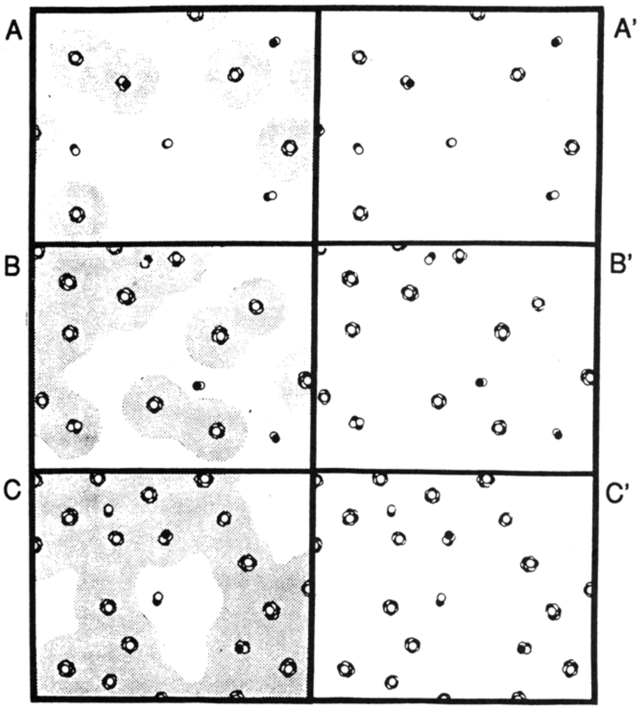

Figure 3. Schematic representation of the morphologies of random ionomers at different ion contents: (A) low ion content; (B) intermediate ion content; (C) high ion content. The shaded areas indicate regions of restricted mobility. A′, B′, and C′ are schematic representations of the spatial arrangement of multiplets considering only electron density factors without regard to chain mobility.

Figure 3. In contrast to other models, there is also no well-defined size or number of ion pairs or multiplets in a cluster.

Another important aspect is that it not necessary to invoke electrostatic interactions between multiplets within a cluster. Although weak electrostatic intermultiplet forces may exist, they are considered to be less important than other factors. The multiplets thus do not "condense" to form the cluster but are close together by virtue of the proximity of the ion pairs on the polymer chain. In this respect, the model differs dramatically from previous theories, which ascribe the driving force for clustering to electrostatic attraction between multiplets.

In random ionomers, there is a distribution of distances between ionic groups along the chain. Very short intergroup distances will probably result in both ions pairs being incorporated into the same multiplet, effectively forming a short loop of polymer chain emanating from the multiplet surface. Beyond this "loopback" distance, the shorter distances between ionic species will tend to be dominant in determining the distribution of intermultiplet distances. This is illustrated schematically in Figure 4. If ion pairs A and C become incorporated into a multiplet, then for ion pairs B and D to be incorporated into another multiplet, the second multiplet must form within the reach of the shorter chain segment, i.e., the length of the chain segment between ion pairs A and B. Thus intergroup distances slightly longer than the loopback distance will be dominant in determining intermultiplet distances and will probably give rise to a most prevalent or preferred spacing. This spacing is thought to be responsible for the position of the "ionic" peak in the SAXS profiles of these materials. However, it should be stressed that a range of intermultiplet spacings is expected, as evidenced by the width of the "ionic" SAXS peak in these materials.[38]

Considering the dimensions of polymer chains and those of multiplets and clusters, it seems reasonable that one

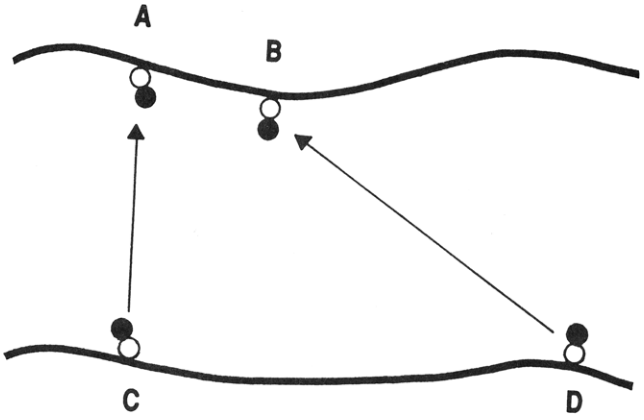

Figure 4. Schematic diagram representing the dependence of intermultiplet distance on the spacing of ionic groups along the polymer chains.

polymer chain may be anchored to a relatively large number of different multiplets and probably even passes through numerous clusters. The intercluster region consists of nonionic chain material in the form of long nonionic segments, loops, and chain ends. In addition, this region may contain lone ion pairs, individual multiplets, or even small aggregates of multiplets with dimensions smaller than those needed for a second T_g to be observed.

In the current model, the presence of clusters is determined by the existence of sufficiently large regions of material with restricted mobility; there is no thermodynamic driving force for phase separation of the clusters. Thus, from a thermodynamic point of view, the term "phase" may not be entirely appropriate to describe the clustered domains. However, the clusters exhibit their own well-defined mechanical characteristics, which are quite reproducible and thus clearly demonstrate phase-separated behavior. The material may be compared to a two-phase system very close to its critical solution temperature. In that case, the differences in composition and properties between the two phases would be expected to be small but quite reproducible, as is the case here. For these reasons, the clusters will be considered to constitute a separate phase for the purposes of this discussion.

The two-phase behavior observed in some ionomers may also be expected to occur in nonionic polymer networks containing multifunctional cross-links. However, this should only occur if the mass and rigidity of the cross-link center is sufficient to cause appreciable immobilization of the polymer chains in the vicinity of the cross-link and provided further that the distance between these cross-link centers is less than twice the persistence length of the polymer.

2.3. Semiquantitative Aspects. SAXS studies on poly(styrene-*co*-cesium methacrylate) with an ion content of 7 mol % indicate an "ionic" peak with a d_{Bragg} of ca. 25 Å.[41,49] If it is assumed for simplicity that the multiplets are uniformly distributed on a cubic lattice in this material with a density of 1.0 g cm^{-3}, the number of ion pairs per multiplet is 5.9 if all of the ion pairs are incorporated into multiplets, 4.4 if 75% of the ion pairs are in multiplets, and 2.9 if 50% are in multiplets.

For the purposes of an illustrative calculation, steric restrictions are assumed to limit the multiplets to an average of ca. 5 ion pairs each, with an average volume of ca. 100 Å^3 in poly(styrene-*co*-sodium methacrylate) containing 7 mol % ions (S0.7MANa). The thickness of the region of restricted mobility surrounding each multiplet is postulated to be of the order of the persistence length of the polymer chain to which the ionic groups are attached. The persistence length of polystyrene in the bulk has been reported as being ca. 10 Å, independent of the temperature.[48] Assuming that all of the material within 10 Å of the surface of the multiplet is appreciably restricted in mobility, the volume of immobilized material per ion pair is approximately 1800 Å^3. Assuming a density of 1 g/mL, at an ion content of 7 mol %, approximately 72 vol % of the material is restricted in mobility if all of the ion pairs are incorporated into isolated multiplets. However, the volume fraction of *clusters* is somewhat less than this for several reasons. Isolated multiplets, or aggregates of multiplets less than 50–100 Å in dimension, would not contribute to the volume of the clustered regions. Lone ion pairs, which are not considered in the above calculation, should also reduce the volume fraction of restricted material. In addition, a significant portion of the clustered material is comprised of overlapping regions of restricted mobility. These overlapping regions occupy the same volume in space, thus making only a single contribution to the volume fraction of the clusters.

The relative areas of the loss tangent peaks for S.07MANa indicate that the clusters occupy on the order of 70 vol % of the material,[40] which corroborates the considerations described above. These considerations were taken into account in formulating the schematic representations of multiplets and clusters in Figures 1 and 3, respectively. It should be emphasized that these considerations are justifiable only for the poly(styrene-*co*-sodium methacrylate) ionomers. Different steric constraints and/or persistence lengths in other ionomers may lead to quite different morphologies. For example, in polystyrene-based ionomers with the same ion content and functional group (i.e., carboxylates), it has been shown that the size of the ionic aggregates ranges from ca. 5 to 25 Å, depending on whether the ionic groups are attached directly to the polymer backbone or to the ends of flexible decyl side chains. Likewise, since the ionic groups in sulfonated polystyrene ionomers are further from the backbone and are thus less sterically hindered than those in analogous poly(styrene–methacrylate) ionomers, the average number of ion pairs per multiplet is also expected to be different. This aspect is discussed in greater detail in a separate publication.[41]

3. Experimental Corroboration

This model either explains or is consistent with an unprecedented range of experimental data for random ionomers. Although it may not address itself to all observed phenomena, the authors are not aware of anything that directly contradicts the model. Most importantly, it reconciles SAXS and dynamic mechanical data and accounts for phase inversion at relatively low ion contents. In this section, some of the specific phenomena accounted for by the model are discussed in somewhat greater detail.

3.1. SAXS Data. The "ionic" SAXS peak is proposed to arise primarily from the most prevalent intermultiplet distance within the clusters. The model allows for *inter*particle but predominantly *intra*cluster scattering at the same time. It should be noted that the SAXS peaks are relatively broad[25–28,50–53] and that a distribution of intermultiplet distances is indicated.[38] Most of these *inter*multiplet distances are *intra*cluster spacings; however, some scattering may also be due to distances between multiplets in neighboring clusters, distances between lone multiplets and those in nearby clusters, or distances between different lone multiplets. These distances are expected to contribute to the observed background scattering intensity. The SAXS profile of these materials is determined *only* by intermultiplet distances; the relative mobility of interstitial chain material has no effect on the scattering. In this regard, the current model is completely consistent with the paracrystalline or liquidlike hard-sphere scattering models previously discussed.[23–25]

The model also accounts for the weak dependence of the Bragg spacing on the ion content of random ionomers.[51] If the multiplets are all assumed to be the same size and uniformly distributed in space, then there is a cube-root dependence of the intermultiplet distance, i.e., d_{Bragg}, on the inverse of the ion concentration.[14] If the number of ion pairs per multiplet increases with increasing ion content, this already weak dependence of d_{Bragg} becomes even weaker, as discussed below. If the number of ion pairs in a multiplet is proportional to the ion content, then the intermultiplet distance remains constant as the ion content is increased. It is recognized that the above relation is only valid for a uniform distribution of multiplets throughout the material and that the current model proposes a distribution of intermultiplet distances with a most prevalent spacing. Nevertheless, the model is in qualitative agreement with the weak dependence of d_{Bragg} on the ion concentration, C, observed for the polystyrene-based ionomers.

The average distance between ionic groups on the polymer chain decreases as the ion content increases, thus favoring the formation of multiplets in closer proximity to one another. This is in accordance with cube-root dependence of d_{Bragg} on C, assuming constant multiplet size. However, the size of each multiplet is limited only by steric factors.[14] At relatively high ion contents, it is expected that the number of ionic groups on adjacent repeat units along the same chain will be higher than that at low ion contents. For example, in perfectly random ionomers, the fraction of ion pairs on adjacent repeat units is approximately 10% for a 5 mol % sample, while ca. 20% of ion pairs in a 10 mol % sample are on a repeat unit that is adjacent to another ion-containing unit. Such vicinal ionic groups may allow more ion pairs to aggregate in a multiplet by effectively reducing the amount of chain material per ion pair, thereby lessening the steric hindrance to aggregation. Hence, the average size of the multiplets is expected to increase slightly with increasing ion content, thus further reducing the dependence of d_{Bragg} on the ion concentration expected from the simple cube-root dependence.

The fact that the SAXS peak persists to temperatures above the T_g of the clusters in some ionomers[52,54] is consistent with the model in that the multiplets remain intact above the cluster T_g in most cases. The high-temperature loss tangent peak is due to the glass transition of the nonionic component of the clusters and *not* decomposition of the multiplets.

No maximum is evident in the SAXS profiles of some polystyrene sulfonate ionomers cast from a 90:10 tetrahydrofuran–water mixture.[52] However, a typical SAXS peak appears rapidly when the sample is heated above its T_g. This phenomenon is completely consistent with the current model. In solution, the ions are expected to be highly solvated and the electrostatic interactions greatly reduced. During the casting process, the most tightly bound solvent molecules, i.e., the water molecules solvating the ions, would be expected to be the last to evaporate. By the time these last water molecules are removed, there is little doubt that the ionomer is below its T_g. The individual ion pairs are thus prevented from associating extensively to form multiplets. As soon as the material is heated above its T_g, the ions are able to associate to form multiplets, which, if present in sufficiently high numbers, give rise to a SAXS peak.

3.2. Dynamic Mechanical Data. At ion contents as low as ca. 2 mol %, a second loss tangent peak appears in the dynamic mechanical data for poly(styrene-*co*-sodium methacrylate) ionomers.[40] This peak has been ascribed to the glass transition of the clusters. In order to exhibit a glass transition, the clustered regions must have minimum dimensions of 50–100 Å. The average diameter of an individual multiplet and surrounding "skin" in S.07MANa is thought to be approximately 25 Å, as depicted schematically in Figure 1. Hence, only very few of the restricted mobility regions surrounding each multiplet need to overlap in order to create a region large enough to exhibit its own T_g.

The fact that two separate peaks are evident in the loss tangent curves for a wide range of random ionomers[3,8] indicates that only two distinct morphological regions are present in these materials. A wide range of morphologies would presumably lead to a single, broad tan δ peak. This is a fundamental feature of the current model in that the loss tangent peaks are postulated to arise from only two morphological regions, viz., unclustered material and clustered material, in which the regions of restricted mobility are large enough to exhibit their own T_g.

As outlined above, the multiplets are expected to be slightly larger and somewhat closer together at higher ion contents. Thus, the mobility of the polymer chains between the multiplets may be expected to decrease with increasing ion content. This provides an explanation for the observed increase in T_g of the clusters with increasing ion content. The growth in the volume fraction of the cluster component at the expense of the unclustered region is responsible for the relative change in the magnitude of the loss tangent peaks with increasing ion content.

In a previous publication, it was suggested that the cluster component becomes dominant and perhaps even continuous at an ion content of ca. 6 mol % in poly(styrene-*co*-sodium methacrylate) ionomers.[40] The current model is unique in being able to account successfully for this phenomenon. As was shown in section 2.3, the clustered component occupies ca. 70 vol % at 7 mol %, and, given the highly irregular shapes of the clusters (see Figure 3), it is not surprising that phase continuity may already exist at ca. 6 mol %.

It has been observed that ionomers derived from polymers in which the chains are relatively *in*flexible do not exhibit two-phase behavior of the type described above. These polymers include materials such as carboxylated phenylated phenylenes[55] and a number of other materials.[56] These materials, by virtue of their high rotational barriers, would be expected to have very long persistence lengths. Therefore, even at very low ion contents, the distance between ionic groups is expected to be less than twice the persistance length. If the ion pairs associate to form multiplets, the mobility of the entire chain would be restricted. Since there would be only negligible amounts of material with unrestricted mobility, two-phase behavior would not be expected.

Ionomers derived from polymers with extremely flexible chains such as polypentenamers only exhibit two-phase behavior at significantly higher ion contents than ionomers derived from polymers with stiffer chains such as polystyrene.[57,58] Small-angle neutron-scattering studies on these materials indicate that the average intermultiplet distance is also somewhat smaller at the onset of clustering than that in polystyrene ionomers.[59] According to the current model, flexible-chain ionomers are expected to have only a thin region of restricted mobility surrounding each multiplet. The multiplets would thus have to be in very close proximity to one another for overlap of the surrounding "skin" to occur. The reduced size of the multiplet plus "skin" would necessitate larger numbers of overlapping regions in order to form clusters with discernible properties. Thus, the onset of two-phase behavior should only occur at significantly higher ion contents than that in ionomers with stiffer chains. Because the multiplets in the clusters have to be closer together in such flexible-chain materials, the Bragg spacing at the point at which two-phase behavior is observed should be less than that in ionomers with stiffer chains at the onset of clustering in those materials.

In ionomers derived from polymers with relatively inflexible chains, the T_g of the material increases with increasing ion content at a significantly higher rate than in ionomers derived from polymers with more flexible chains, provided that the T_gs of the two host polymers are reasonably similar. For example, the T_g of sulfonated poly(aryl ether ether ketone)[56] increases as the inverse equivalent weight increases at a rate of 9.4×10^4 °C g mol^{-1}, while for sulfonated polystyrene,[60] the rate is 3.4×10^4 °C g mol^{-1}. The T_gs of the two host polymers are ca. 150 and 100 °C, respectively. As described above, at low ion contents, the T_g of a rigid-chain ionomer is not increased by cross-linking effects as in more flexible ionomers but by the immediate onset of clustering. Thus, it is not surprising that the T_g of the material increases rapidly as the ion content is increased. It should be noted that when the behavior of flexible ionomers is contrasted with more rigid-chain ionomers, it is essential not to make comparisons on the basis of mole percent ions because the repeat units may be significantly different in size and mass. In such cases it is better to compare the ionomers on the basis of equivalent weight.

In polystyrene-based ionomers there is a range of ion contents over which two-phase behavior is observable. At very low ion contents (<1 mol %), the intermultiplet distance is significantly larger than twice the persistence length, which minimizes overlap and thus results in single-phase behavior. At high ion contents (>15 mol %) virtually all of the material is "overlapped" or restricted in mobility and may therefore be considered to be clustered, as evidenced by the almost complete absence of a low-temperature loss tangent peak.[40] This illustrates one of the key features of the model, i.e., that approximately twice the persistance length between multiplets is required for two-phase behavior to be observed. At much larger intermultiplet distances, no overlap of restricted mobility regions occurs, thus resulting in only a single observable T_g. This is the case for flexible-chain ionomers such as polypentenamers at ca. 6 mol %.[57] At intermultiplet distances much shorter than twice the persistence length, the entire sample may be effectively clustered and thus exhibit only single-phase behavior. This is the case for relatively inflexible-chain ionomers or in polystyrene ionomers at very high ion contents.

The fact that the loss tangent peak associated with the clusters is significantly broader than the low-temperature peak[40] may be accounted for by the range of mobilities of the polymer chains within the clusters. A high degree of overlap of the regions of restricted mobility surrounding each multiplet will result in lower chain mobility than in the case of less overlap. A range of intermultiplet distances within the clusters is indicated by SAXS studies, thus giving rise to different extents of overlap and chain mobilities.

Although not a feature of random ionomers, the model also successfully explains the absence of two-phase behavior in noncrystalline telechelics with relatively high molecular mass.[61] Carboxy-terminated polystyrenes with number-average molecular weight, M_n, greater than 5900 do not show any breakdown of the time-temperature superposition in stress-relaxation studies, thus indicating the presence of only a single phase. The ionic aggregates in these materials are likely to be too far apart for the region of restricted mobility surrounding each multiplet to overlap. However, carboxy-terminated polystyrene telechelics with number-average molecular weights of less than 3300 show a clear breakdown of the time-temperature superposition in stress-relaxation studies.[61] This evidence of two-phase behavior may be due to the fact that, in these materials, the multiplets are close enough to each other for overlap of the restricted mobility regions to occur.

Steric limitations on multiplet size are less significant in telechelics and long side-chain ionomers than in random ionomers. This results in larger multiplets, which must contain some nonionic chain material unless unusual geometries develop. These large aggregates are clearly not clusters and may be thought of as large multiplets, although they may be slightly different from the classical multiplet encountered in random ionomers in that they contain some nonionic material. It should be noted in this regard that halato telechelics, which are widely regarded as being good models for multiplet formation in random ionomers, are clearly *not* good models with respect to clustering in random ionomers.

3.3. Electron Microscopy. Despite the fact that dynamic mechanical data have indicated that the minimum dimensions of the clusters must be 50–100 Å, extensive electron microscopy studies on random ionomers have failed to detect any evidence of features of this size.[13,63] The current model provides a simple explanation for this phenomenon. Because microscopy techniques cannot distinguish between the regions of restricted mobility in the ionomer from the regions of higher mobility, it is not possible to detect the clusters with this approach. Resolution on the order of a few angstroms would be required in order to see the multiplets.

Because the ionic aggregates in halato telechelics are substantially larger than in random ionomers due to reduced steric hindrance, the ionic aggregates in telechelics should be more readily detected by electron microscopy techniques. Indeed, it has recently been reported that multiplets in telechelics have been observed directly by STEM methods.[63] However, it should be borne in mind that multiplet formation in samples cast from solution may be significantly less extensive than that in compression-molded samples, as discussed in section 3.1.

3.4. Plasticization Effects. Many studies have been performed on the effects of both polar and nonpolar plasticizers on the properties of random ionomers.[12,44] In this section, some of the observed effects are discussed in relation to the current model.

3.4.1. Nonpolar Plasticizers. Nonpolar plasticizers have been widely reported as being able to plasticize both the unclustered and clustered regions leading to a marked, and sometimes parallel, decrease in the cluster T_g and the T_g of the more mobile regions.[12,45] One explanation for the decrease in the T_g of the cluster component on addition of nonpolar plasticizer[44] has been the so-called "thermal-stress" effect, according to which the T_g of the dispersed "hard" phase is assumed to decrease because of its proximity to a "soft" phase in a fashion similar to that encountered in some block copolymers.[64] Another possible explanation may be the incorporation of the nonpolar plasticizer into the clusters. However, most previous models are inconsistent with this explanation because the nonpolar diluent would not be expected to diffuse into regions of high polarity. The current model successfully accounts for the reduction in cluster T_g on nonpolar plasticization, without recourse to the thermal-stress effect or plasticization of the ionic domains. Clearly the nonpolar diluent is able to plasticize the regions of restricted mobility between the multiplets in the cluster just as easily as the nonpolar material in the regions of higher mobility. There is no reason for the plasticizer to concentrate more in one component than in the other. Because the T_g of the clusters is determined by the polymer chains between the multiplets and not the multiplets themselves, it is not surprising that the T_gs of the clustered and unclustered regions often decrease in parallel on addition of nonpolar plasticizer.

3.4.2. Polar Plasticizers. Polar plasticizers selectively cause a reduction in the T_g of the clusters in random ionomers.[12,65–71] This is completely consistent with the current model in that polar plasticizers are expected to be incorporated into the multiplet, shield the electrostatic interactions between the ion pairs, and introduce more free volume, thus reducing the firmness with which the ion pairs in the multiplet are anchored. This results in increased mobility of the hydrocarbon chains attached to the ion pairs and thus a decrease in the T_g of the regions of restricted mobility.

In a study of the dynamic mechanical properties of poly(styrene-*co*-sodium methacrylate) plasticized with glycerol, it was observed that the tan δ peak associated with the unclustered material increased in magnitude with increasing glycerol content.[71] This occurs because plasticization effectively increases the mobility of the chains attached to the multiplets and thus reduces the volume of the restricted mobility region surrounding each multiplet. Hence, some of the material in the clusters effectively becomes part of the unclustered region, thereby increasing the volume fraction of the unclustered regions and reducing the volume fraction of the clusters. Although the tan δ data for the clusters were not obtained in the plasticization study, the magnitude of the tan δ peak is expected to decrease with increasing amounts of a polar diluent.

Sufficient amounts of a polar plasticizer may completely obliterate the mechanical characteristics usually associated with two-phase behavior.[12,44,72] This occurs because the plasticizer may reduce the firmness with which the ion pairs are anchored to such as extent, that the effective thickness of the regions of restricted mobility within the cluster is reduced to the point where overlap no longer occurs, hence destroying the mechanical features associated with the cluster.

4. Predictions

The proposed model reconciles a wide range of phenomena observed in random ionomers, notably in terms of relating molecular parameters to two-phase behavior. Insofar as these have been verified experimentally, they have been discussed in section 3. Several, however, have not yet been treated experimentally, and these are listed as predictions in this section. The accuracy of these predictions will provide an excellent test of the validity and generality of the model.

Usually, the cluster tan δ peak and the "ionic" SAXS peak are either both present or both absent in random ionomers, provided that sufficient contrast exists between the multiplets and the bulk polymer to observe a scattering peak. However, according to the current model, it may be possible to observe only the SAXS peak in some systems. Nonpolar plasticization of random ionomers introduces additional free volume to the system and hence effectively increases the mobility of the polymer chains. Consequently, this reduces the thickness of the region of restricted mobility surrounding each multiplet. If sufficient plasticizer is added, these regions may be reduced in thickness to the point where they no longer overlap. In such an instance the mechanical properties associated with the clusters would no longer be evident. However, the SAXS peak should still persist.

Very high levels of polar plasticizer may result in solvation of the ion pairs within the multiplets, thereby reducing the electrostatic interactions between the ion pairs to the point where the entropic and elastic forces opposing multiplet formation are able to overcome the electrostatic attractions and even pull the multiplet apart. In this event, not only the mechanical features associated with the clusters but also the SAXS peak should disappear.

Another prediction of this model is that telechelics derived from polymers with very stiff chains (the persistence length is greater than or equal to the half of the contour length of the chain) should exhibit very different mechanical behavior from telechelics derived from more flexible chains in that the entire sample should be restricted in mobility and therefore behave as if it were clustered. This phenomenon should only be observed if the morphologies of the two telechelic ionomers are similar. Analogous behavior is expected in ABA blocks in which the length of the middle nonionic segment is less than or equal to twice the persistance length.

Finally, it is predicted that it may be possible to determine the persistence length along the contour path between ionic groups from dynamic mechanical and SAXS data for materials that contain rigid multiplets and exhibit two-phase behavior. As the ion content is increased in such materials, a point is reached at which the cluster tan δ peak becomes dominant. The d_{Bragg} measured at this ion content should give a reasonable indication of twice the persistence length of the polymer plus the diameter of a multiplet if the ionic groups are attached directly to the polymer backbone. The diameter of a multiplet may be estimated to within a few angstroms, thus allowing a fairly precise approximation of the persistence length. A great deal of experimental work on ionomers would be needed to verify this hypothesis.

5. Conclusions

Despite extensive studies on random ionomers, the exact structures of the ionic aggregates responsible for the unique physical properties of these materials have not yet been fully elucidated. A number of models have been proposed, none of which satisfactorily account for all of the observed experimental phenomena. Recent evidence of phase inversion at relatively low ion contents, coupled with SAXS results that suggest a continuity of morphology between telechelics and random ionomers, has led to the development of a new model, which successfully accounts for a wide range of experimental observations. The model is in complete agreement with the SAXS data as interpreted by previous hard-sphere models.

The model is based on the formation of multiplets. However, in contrast with previous cluster models, it is not necessary to invoke electrostatic interactions between multiplets in order to explain the existence of clusters. An important feature of the model is a proposed region in which the hydrocarbon polymer chain segments surrounding each multiplet experience appreciable restrictions in mobility. The thickness of this region is postulated to approximate the persistence length of the host polymer. An individual multiplet raises the T_g of the material by effectively acting as a large cross-link, but the restricted region surrounding such an individual multiplet is not large enough to exhibit its own T_g. Only when a number of these regions overlap to form a relatively large contiguous region of restricted mobility with its own T_g is the region considered to constitute a cluster. The clustered regions, which are likely to be highly irregular in shape, have no upper limit on the number of ions pairs or multiplets that they may contain. The clusters behave as if they were phase-separated from the regions of more mobile segmental motion in that they exhibit their own T_g, which is significantly higher than the T_g of the unclustered component. In these regions also, one would expect a most prevalent intermultiplet spacing. This spacing accounts for the characteristic "ionic" peak in the SAXS profiles of these materials above a certain ion content.

A wide range of other experimentally observed phenomena are also accounted for by the model. These include the weak dependence of the Bragg distance on the ion content, phase inversion at relatively low ion contents, the inability to see clusters by electron microscopy techniques, the absence of two-phase behavior in "stiff-chain" ionomers, and the effects of both polar and nonpolar plasticizers.

The model also leads to several predictions, including the possible observance of a SAXS peak in the absence of a tan δ peak in some systems, complete disruption of the multiplets at very high levels of polar plasticizers, a difference in mechanical properties of flexible-chain and stiff-chain halato telechelics, and the possible determination of persistence lengths from dynamic mechanical and SAXS data.

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