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Viscoelastic and Morphological Study of Ionic Aggregates in Ionomers and Ionomer Blends

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ABSTRACT: Aggregation of the ionic groups in blends of sulfonated polystyrene (SPS) with ethyl acrylate/4-vinylpyridine and styrene/4-vinylpyridine copolymers was investigated by dynamic mechanical thermal analysis (DMTA) and small-angle X-ray scattering (SAXS). Viscoelastic measurements show the existence of a high-temperature loss peak, similar to the peak observed in ionomers. However, the temperature of the transition is depressed relative to the parent ionomers due to internal plasticization. The presence of ionic aggregates was confirmed by calculating the average network functionalities and by the failure of frequency-temperature superposition. Activation energies for the high-temperature transition are related to the relative strengths of the interactions, which is consistent with the transition being due to motion of the ionic groups. SAXS measurements show that the "ionic peak" present in ionomers is destroyed upon blending. The data are discussed in terms of models for ionomer morphology.

Introduction

Ionomers are defined as hydrocarbon polymers containing 10% or less ionic groups. One of the biggest classes of ionomers is that based on copolymers of ethylene and methacrylic acid.[1] One complication in interpreting the behavior of these ionomers is the presence of crystallinity. As a simpler system, sulfonated polystyrene ionomers have been studied extensively in recent years.[2] Other ionomers include those based on EPDM, poly(phenylene oxide), poly(ether ether ketone), polypentenamer, and segmented polyurethanes, to name a few.[2]

Because of the difference in polarity between the ionic groups and the hydrocarbon chains, there is an electrostatic driving force for aggregation of the ionic groups. The first theory describing this aggregation is that due to Eisenberg.[3] In his work, a "multiplet" is defined as an aggregate in which the ions are in contact with each other with no intervening hydrocarbon chain. A "cluster" is an aggregate of multiplets which contains some hydrocarbon chains. The size of the clusters is determined by a balance of the forces resulting from electrostatic attraction between multiplets and elasticity of the polymer chains. However, the morphology of the clusters is not described by this theory.

Viscoelastic measurements on ionomers have shown the existence of a high-temperature loss peak, which has been termed the ionic cluster transition.[1,2] This transition is interpreted as being due to motions within the clusters, although the exact nature of the motion is not clear. Some investigators have claimed that it is due to a glass transition within the cluster,[4] while others have explained it as being due to dissociation and motion of the ionic groups.[2] Small-angle X-ray scattering measurements have shown the existence of a peak at a scattering vector q between 1 and 3 nm^{-1} and a low-angle upturn.[5-7] The interpretation of these features is model dependent. The three major models of ionomer morphology are the core-shell model of MacKnight et al.,[5] the hard-sphere liquid-like interference model of Yarusso and Cooper,[6] and the restricted mobility model of Eisenberg et al.[8]

One of the first models to describe the scattering features was that of MacKnight et al.[5] Based on a Guinier analysis of the upturn, a Porod analysis at high angles, and a radial distribution function fit to the data, they proposed a core-shell model for the morphology. In this model the multiplets aggregate into an ionic core containing some hydrocarbon chains, surrounded by a shell depleted in ions. Beyond the shell the matrix contains a few isolated multiplets. The key feature of the core-shell model is that it attributes the scattering to intraparticle effects. In particular, the ionic scattering peak is due to the preferred distance established by the depleted shell region.

On the other hand, an interparticle scattering model has been proposed by Yarusso and Cooper.[6] Fits of theoretical models to the experimental scattering data showed that a better fit is obtained with a hard-sphere liquid-like interference model than with the core-shell model. In the hard-sphere liquid-like interference model the clusters are arranged with a liquid-like degree of order, and the peak occurs due to discrete scattering effects between clusters, while the upturn is attributed to some undefined inhomogeneity in the distribution of the clusters. This model also fits scattering data obtained during the deformation of ionomers.[9]

The third major model of ionomer morphology has been proposed recently by Eisenberg et al.[8] In their restricted mobility model the cluster is considered to consist of regions of hydrocarbon chains that are restricted in mobility due to the cross-linking effect of the multiplets. This is also an interparticle scattering model, with the ionic peak resulting from interference effects between multiplets.

It is well known that the ionic peak in SAXS and the ionic transition in DMTA are affected by the type of cation, the amount of ionic groups, and the presence of low molecular weight compounds.[1,2] Investigations of plasticization in sulfonated polystyrene ionomers showed that either the polar ionic cluster or the nonpolar parent matrix could be selectively plasticized, depending on the dielectric constant of the solvent used.[10-12] Studies on dielectric relaxations in ethylene ionomers showed that the addition of the complexing agent 1,3-bis(aminomethyl)cyclohexane (BAC) to transition metal neutralized ionomers enhanced cluster formation.[13]

As part of an extensive study of miscibility enhancement in ionomer blends, Simmons and Eisenberg noted that blends of ethyl acrylate/lithium acrylate copolymers with poly(ethylenimine) (PEI) showed a DMTA cluster transi-

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Table 1. Characteristics of Blend Precursors

polymer	ionic content (mol %)	M_n	M_w
0SPS	0	100 000	250 000
2HSPS	1.71	100 000	250 000
5HSPS	5.7	100 000	250 000
8HSPS	7.6	100 000	250 000
2ZSPS	2.1	100 000	250 000
5ZSPS	5.5	100 000	250 000
7ZSPS	7.25	100 000	250 000
0EAVP	0	230 000	890 000
2EAVP	2.4	230 000	730 000
5EAVP	5.2	201 000	406 000
10EAVP	10.6	161 000	315 000
2SVP	2.2	27 800	280 000
5SVP	4.2	4 500	16 500
8SVP	7.4	13 500	57 800

tion that depended greatly on the PEI content.[14] However, no detailed analysis was performed. This work for the first time discusses in detail the effect of blending on ionic clusters. In addition it is hoped that the study of clustering in blends will provide some insight into the nature of clustering in ionomers.

Experimental Section

Polymer Synthesis. The sulfonated polystyrenes in both the acid (HSPS) and zinc neutralized (ZSPS) forms were kindly provided by Exxon Research and Engineering Co. Sulfonation levels and molecular weights are given in Table 1.

The copolymers of ethyl acrylate and 4-vinylpyridine (EAVP) were prepared by free-radical polymerization in solution. The reactivity ratios for this polymerization are $r_{EA} = 0.29$ and $r_{VP} = 2.58$.[15] A typical polymerization consisted of reacting 300 g of monomer and 7 g of AIBN in 700 mL of methanol at 60 °C for times varying from 20 to 90 min, depending on the pyridine content. Conversions for the polymerizations were approximately 20–30%. Styrene/4-vinylpyridine copolymers (SVP) were prepared by free-radical polymerization in the bulk. Reactivity ratios for this polymerization have been reported as $r_S = 0.54$ and $r_{VP} = 0.70$.[16] A typical polymerization consisted of reacting 150 g of monomer and 0.375 g of AIBN at 60 °C for 4 h. Total monomer conversions for the reaction were approximately 10–20%. The polymers were purified by precipitating into water and drying for 3 days at 60 °C under vacuum. Pyridine contents determined by elemental analysis and molecular weights determined by GPC based on polystyrene standards are given in Table 1.

The conditions used for these polymerizations are expected to result in some compositional heterogeneity. Calculations for the EAVP copolymers show that for the EAVP copolymer containing 5% 4-vinylpyridine, the composition of the initially formed polymer is approximately 5% 4-vinylpyridine, while the polymer formed at the end of the reaction contains approximately 2% 4-vinylpyridine.[17] We have previously discussed the effect of this compositional heterogeneity on the morphology of styrene and ethyl acrylate domains in SPS/EAVP blends.[17,18] For the purposes of the present study any affects of this compositional heterogeneity will likely be subtle and will not affect the general results or conclusions.

Blending. All blends were prepared to have equal numbers of sulfonate and pyridine groups. The acid blends were prepared according to the procedure of Smith and Eisenberg.[19] The HSPS and EAVP (or SVP) were dissolved separately in THF at a concentration of 1% (w/v). The EAVP (or SVP) solution was added to the HSPS solution dropwise over a period of about 45 min while stirring, and stirring was continued an additional 30 min after addition ended. In all cases a gel was formed, and this gel was removed from the solvent. The zinc blends were prepared in the same fashion, except that DMF was used as the solvent due to limited solubility of the zinc ionomers in THF, and the blends were isolated by precipitating into distilled water. All blends were dried at 60 °C for 3 days under vacuum. Infrared spectra showed no evidence of any residual DMF. The nomenclature of the blends is as follows: the first number indicates the sulfonation level of the SPS in mole percent, the letter indicates the counterion, and the second number indicates the pyridine content of the 4-vinylpyridine copolymer in mole percent. Blends whose designation ends with the letter "S" contain the styrene/4-vinylpyridine copolymer, while those with no letter at the end contain the ethyl acrylate/4-vinylpyridine copolymer. Characteristics of the blends are given in Table 2.

Table 2. Characteristics of Blends

blend desig	counterion in sulfonated polystyrene	sulfonation level in sulfonated polystyrene (mol %)	vinylpyridine content in copolymer (mol %)	wt frac of vinylpyridine copolymer in blend
00		0	0	0.50
2H2	H^+	1.71	2.4	0.40
5H5	H^+	5.7	5.5	0.50
8H10	H^+	7.6	10.5	0.40
2Z2	Zn^{2+}	2.1	2.4	0.45
5Z5	Zn^{2+}	5.5	5.1	0.51
7Z10	Zn^{2+}	7.25	10.6	0.37
2H2S	H^+	1.71	2.2	0.23
5H5S	H^+	5.7	4.2	0.56
8H8S	H^+	7.6	7.1	0.49
2Z2S	Zn^{2+}	2.1	2.2	0.48
5Z5S	Zn^{2+}	5.5	4.2	0.55
7Z8S	Zn^{2+}	7.25	7.4	0.47

Dynamic Mechanical Thermal Analysis (DMTA). DMTA was performed on a Polymer Laboratories DMTA operating in the shear mode. Samples were compression molded into disks approximately 1 mm thick by 12 mm in diameter. The molding temperatures were the minimum temperatures needed to cause flow, which were 175 °C for the HSPS's and all SPS/EAVP blends, 200 °C for the SPS/SVP blends, and 250 °C for the ZSPS's. Samples were held at the molding temperature for 6 min, followed by quenching to room temperature. DMTA thermal scans were done from 50 to 300 °C at 2 °C/min at five frequencies (0.33, 1, 3, 10, and 30 Hz) with a 64-μm peak-to-peak displacement. The Polymer Laboratories DMTA multiplexes the frequencies, so a single scan generated the curves at all five frequencies. Two different samples were run for each material to ensure reproducibility.

It is important to note that the measured values for the modulus in the glassy region will be significantly lower than expected due to an artifact of the instrument. The Polymer Laboratories DMTA only operates within a certain range of stiffness. Samples which are too stiff, as is the case for these samples in the glassy state, give modulus values which are unrealistically low. Once the samples have gone through the glass transition, their stiffness drops dramatically, and the true storage modulus can be measured. Thus, modulus values will only be accurate above the glass transition, and only so long as the modulus remains above 10^2 Pa.

DMTA isothermal scans were done on the ZSPS's and the SPS/SVP blends. Isotherms were measured at every 10 °C from 70 to 270 °C, with seven frequencies at each isotherm (0.033, 0.1, 0.33, 1, 3, 10, and 30 Hz). The samples were allowed to equilibrate for 15 min at each temperature before measurement. Superposition of the isotherms was done empirically by shifting the tan δ isotherms to give the maximum overlap. The modulus isotherms were then superposed by applying arbitrary vertical shifts to the data.

Small-Angle X-ray Scattering (SAXS). Samples for SAXS measurements were prepared by compression molding into bars 20 mm × 5 mm × 1.5 mm under the same conditions as described above for the DMTA measurements. The samples were then annealed at 150 °C for 24 h followed by slow cooling over several hours to room temperature.

SAXS measurements were done on a Rigaku-Denki camera using slit collimation and nickel-filtered Cu Kα X-rays generated by a sealed tube source operating at 45 kV and 33 mA. The scattered X-rays were detected using a scintillation counter and a pulse height analyzer. The counter was placed on a stepper motor, and the scans were conducted from 0.2 to 6.5° 2θ in 0.05° steps with a 600-s acquisition time at each angle. The smeared data were corrected for parasitic scattering, absorption, and irradiated sample volume. Slit-smearing corrections were done using the approach of Glatter.[20]

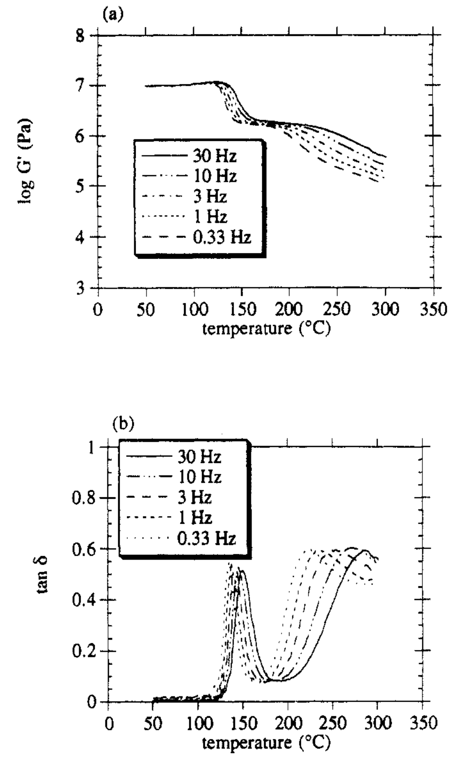

Figure 1. Multifrequency DMTA plots of (a) storage modulus and (b) tan δ for 5ZSPS in shear.

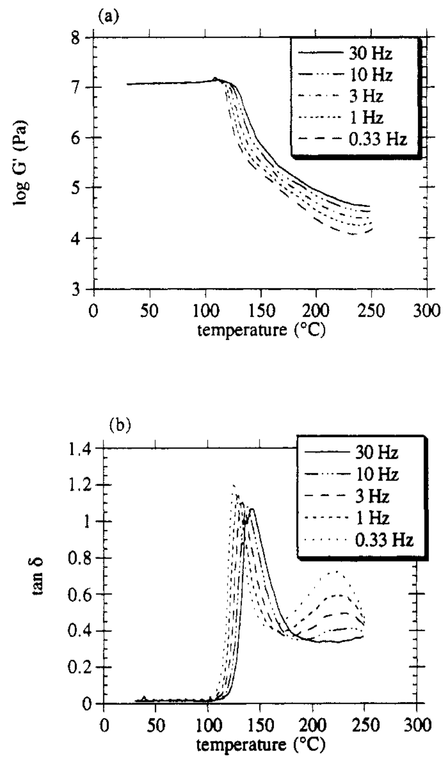

Figure 2. Multifrequency DMTA plots of (a) storage modulus and (b) tan δ for 8HSPS in shear.

Results and Discussion

Viscoelasticity. Dynamic mechanical measurements have been used extensively to examine aggregation in ionomers.[21-23] Ionomers exhibit a high-temperature loss peak, which has been called the ionic cluster transition. The storage modulus exhibits a plateau, reminiscent of the plateau seen in cross-linked systems. These features are evident in the multifrequency plot for 5ZSPS shown in Figure 1. The high-temperature loss peak has been interpreted as being due to motions within the ionic aggregates, although the exact nature of these motions is not clear. They have been described as the glass transition of hydrocarbon chains associated with the cluster[4] or alternatively as being due to the thermal breakup and subsequent motions of the ionic groups themselves.[2] The plateau in the storage modulus is generally described as being a rubbery plateau, due to ionic cross-linking by the aggregates.[23] In addition to the cross-linking effect, Connolly has described the plateau as being due to the two-phase nature of ionomers, with the aggregates acting as reinforcing filler particles.[22]

Figure 2 shows the modulus and loss curves for 8HSPS. There is some question over whether or not the acid form of sulfonated polystyrene shows an ionic cluster transition. Most authors state that HSPS does not form clusters because the hydrogen bonding between sulfonic acid groups does not provide a sufficient driving force for aggregation.[1,24] More recently, however, there have been a few reports of a cluster transition in HSPS.[22,25] The data in Figure 2 show an apparent loss peak at approximately 220 °C, but careful examination shows that the peak is independent of frequency, in contrast to the frequency dependence for the cluster transition seen in Figure 1. This apparent peak is more likely caused by dimensional changes of the sample due to flow. The Polymer Laboratories instrument measures the stiffness of the sample, which is the product of the modulus and a geometric factor. If the sample dimensions change during a scan, then the stiffness will change, which is interpreted by the instrument as a change in both storage and loss modulus. The apparent loss peak results from the change in the sample during the time it flows and changes dimensions, since such flow results in a new loss mechanism. In fact, by the end of the scan the sample has flowed out from between the clamps, which would result in a drop in the apparent modulus and the appearance of a loss peak. Thus, it might be concluded that the HSPS's used in this study do not show a cluster transition.

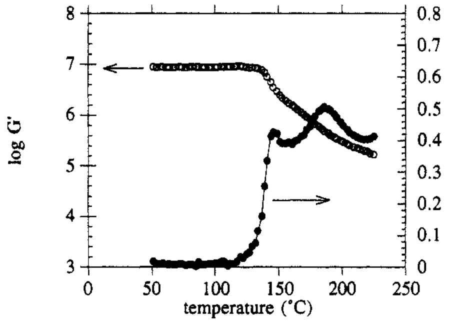

Figure 3. log G' and tan δ at 1 Hz for blend 7Z8S.

For an illustration of the quality of the data, Figure 3 shows the storage modulus and loss curves for blend 7Z8S at 1 Hz. In all subsequent figures the data points are not shown for clarity. The loss curves for all the blends and the ZSPS ionomer at 8% substitution level at 1 Hz are shown in Figure 4. The arrows in the figure indicate the cluster transition. Curves at other substitution levels are similar. Figure 5 shows the cluster transition temperatures for all the materials, and the values are listed in Table 3. Blending obviously has a profound effect on the cluster transition temperature in the zinc-neutralized materials. The difference in the transitions between ZSPS and ZSPS/SVP blends range from 40 to 60 °C and is due to the addition of the pyridine substituent. The pyridine modifies the interactions between ionic groups within the cluster by changing the strengths of the interactions. Since the cluster transition is due to motion and dissociation of ionic

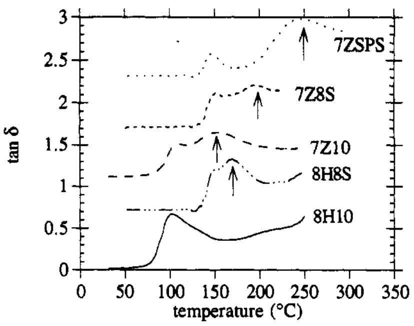

Figure 4. tan δ at 1 Hz in shear at the 8% substitution level. The curves have been shifted vertically for clarity. Arrows indicate the cluster transitions.

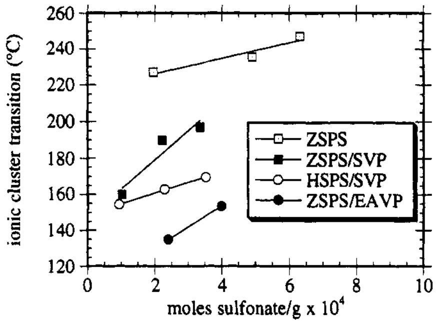

Figure 5. Ionic cluster transition temperatures.

Table 3. Ionic Cluster Transition Temperatures and Activation Energies

material	T_{ionic}[a] (°C)	E_a (kJ/mol)
2ZSPS	227.0 ± 2.0	161.8 ± 5.0
5ZSPS	235.5	157.9
7ZSPS	247.0	169.8
2Z2		
5Z5	134.9	124.8
7Z10	153.7	146.2
2Z2S	160.0	220.9
5Z5S	189.8	192.2
7Z8S	197.0	220.7
2H2S	154.5	288.1
5H5S	162.8	299.6
8H8S	169.8	305.0

[a] Taken as the position of the peak in tan δ at 1 Hz.

groups, the changes in these interactions caused by the pyridine lower the transition temperatures. The ZSPS/EAVP blends exhibit cluster transitions another 40 °C lower than the ZSPS/SVP blends due to the plasticization effect of the ethyl acrylate segments incorporated into the cluster. Poly(ethyl acrylate) has a much greater mobility than polystyrene at these temperatures, since the temperature of the transition is approximately 170 °C above the T_g for poly(ethyl acrylate) as opposed to only 50 °C above T_g for polystyrene. Thus, the ethyl acrylate segments are expected to be an efficient plasticizer for the clusters. The amount of the decrease in the transition temperature in the ZSPS/EAVP blends is similar to what has been seen when ionomers are plasticized with a polar small-molecule plasticizer such as glycerol, which is selective for the clusters.[10-12]

There is apparently a fairly strong dependence of the cluster transition temperatures on substitution level for the ZSPS/SVP and ZSPS/EAVP blends. The dependence in ZSPS/EAVP blends is due to the amount of ethyl acrylate incorporated into the clusters. For a given number of ionic groups in a cluster, a lower substitution level will necessarily have more ethyl acrylate present, because there are longer ethyl acrylate segments between the ionic groups. Thus the plasticization effect will be stronger at

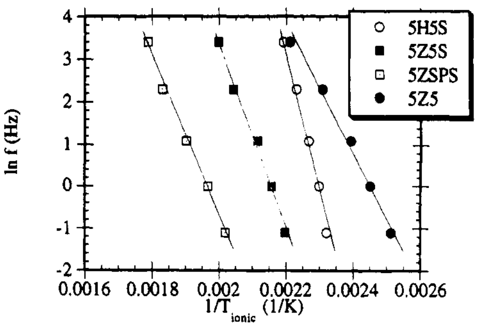

Figure 6. Arrhenius plots of the ionic cluster transition for blends and ionomers at the 5% substitution level.

a lower substitution level. The absence of a transition in blend 2Z2 may be due to two effects. The first is that the effect of plasticization is so strong that the cluster transition falls below the glass transition. The second is that the addition of 50% EAVP reduces the concentration of ionic groups to below the threshold for aggregation. For example, we note that ZSPS with 0.5% sulfonation does not show a cluster transition.[22] It is not clear why there should be a substitution level dependence of the transition temperatures for the blends that do not contain ethyl acrylate based on plasticization. The Eisenberg model for ionomer morphology may provide an explanation, in that the mobility of polymer chains in the regions of restricted mobility decreases as the total volume of ionic groups increases, resulting in an increase in the cluster transition temperature.

As was stated previously, the HSPS's used in this study do not show a cluster transition. However, the HSPS/SVP blends do show a cluster transition. The driving force for aggregation in ionomers is electrostatic interactions between the charged species.[3] In blends containing HSPS the interaction occurs via proton transfer from the sulfonic acid to the pyridine, resulting in a sulfonate anion and a pyridinium cation.[26-29] One might think of this situation as a double ionomer, in which the neutralizing species for one ionomer is the other ionomer. The resulting electrostatic interactions result in the formation of aggregates. A similar effect has been seen by Yano et al. in transition metal neutralized ionomers using dielectric measurements.[13] The neat ionomer does not show a cluster transition, but the ionomer with an added complexing agent does show a cluster transition. The action of the complexing agent is apparently to increase the charge density on the transition metal, resulting in a stronger electrostatic driving force for aggregation.

Activation energies for the cluster transitions can be determined from the multifrequency loss plots. Typical Arrhenius plots for all materials at the 5% substitution level are shown in Figure 6. The plots are fairly linear, although the limited frequency range makes it impossible to determine whether or not the data actually follow an Arrhenius-type of dependence.

The values for the activation energies are shown in Figure 7 and listed in Table 3. It has been proposed that flow in ionomers occurs via an ion-hopping mechanism in which the ionic groups dissociate from the clusters.[30] The rate at which this dissociation occurs depends on the strength of the electrostatic interactions between the ionic groups and thus should be related to their relative charge densities. The order in which the activation energies occurs can be rationalized on this basis. The acid blends have complete charge separation between the sulfonate anion and pyridinium cation,[31] resulting in a high charge density and the highest activation energies. In the zinc blends the

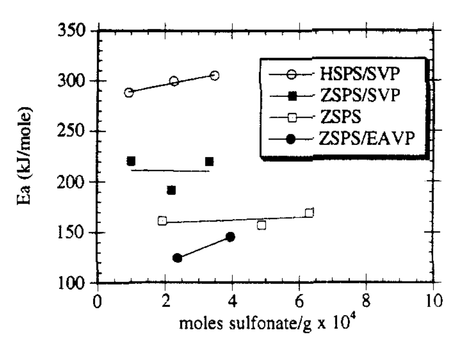

Figure 7. Ionic cluster transition activation energies.

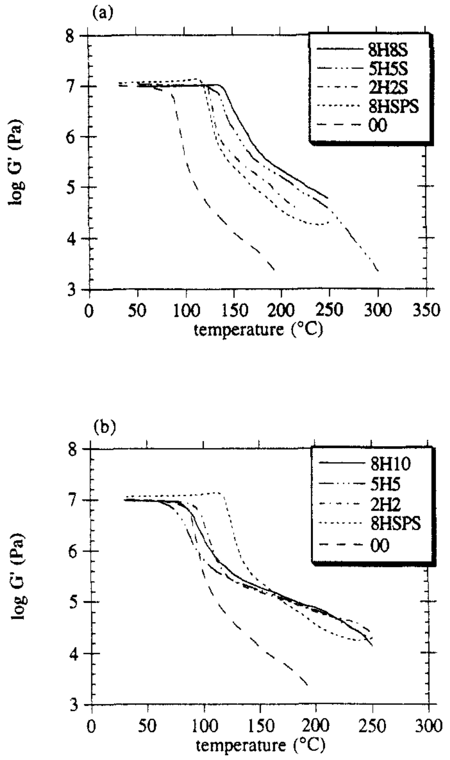

Figure 8. Shear storage moduli at 1 Hz for (a) acid styrene/styrene and (b) acid styrene/ethyl acrylate blends. Curves have not been corrected for machine compliance at low temperatures.

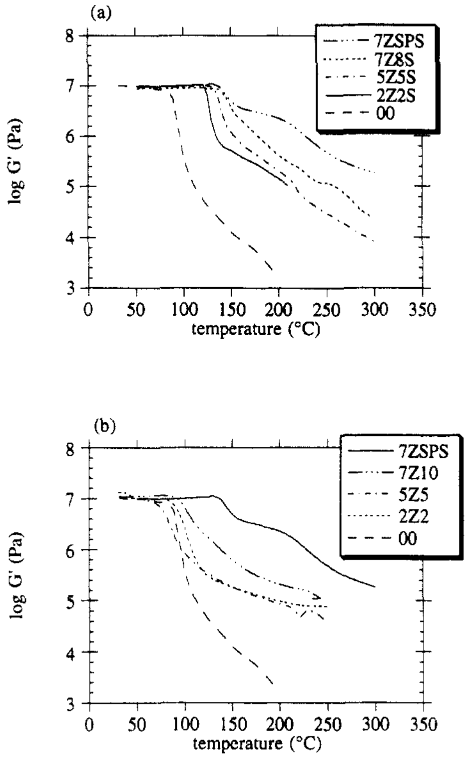

Figure 9. Shear storage moduli at 1 Hz for (a) zinc styrene/styrene and (b) zinc styrene/ethyl acrylate blends. Curves have not been corrected for machine compliance at low temperatures.

zinc ion is coordinated to pyridine,[29] resulting in partial charges on the zinc and the pyridine and a lower charge density than in the acid blends. In the zinc ionomer the zinc is coordinated to water,[29] which is a weaker ligand than pyridine, and so the charge separation is even lower. The ZSPS/EAVP blends are affected by the higher dielectric constant of the ethyl acrylate, which partially screens the charges and reduces the electrostatic interactions.

Since the activation energies for the cluster transitions are clearly determined by the electrostatic interactions between ionic groups, the results support the idea that the cluster transition is a result of the dissociation and motion of the ionic groups.

The storage modulus curves for all materials at 1 Hz are shown in Figures 8 and 9. The modulus curves for the acid blends in Figure 8 show that the modulus is increased due to the presence of ionic cross-links. The curve for 8HSPS is higher than for the unfunctionalized blend due to hydrogen-bonding interactions between the sulfonic acid groups. The styrene/styrene acid blends all have higher moduli than 8HSPS, even at the 2% substitution level, and the modulus increases with the number of interactions. This is the behavior that would be expected if the interactions act as cross-links. It is important to note, however, that there is no rubbery plateau, as there would be for a covalently cross-linked rubber. This is because the difference between the glass transition and the cluster transition for the HSPS/SVP blends is so small that any plateau would not be detected.

The moduli for the HSPS/EAVP blends are lower than for 8HSPS. This is because the ethyl acrylate component lowers the glass transition of the blend significantly compared to 8HSPS. The absence of a plateau is because the HSPS/EAVP blends do not exhibit a cluster transition, which indicates that the clusters, which act as the cross-links, are not stable at all temperatures above T_g.

The behavior of the zinc blends shown in Figure 9 is very different. The plateau that is present in the ionomer is no longer present in the blends, and the modulus curves lie below the curve for the ionomer. The absence of the plateau is again due to the small difference between the glass transition and the cluster transition. The drop in the modulus compared to the ionomer results from a change in the state of aggregation. The exact nature of this change will be discussed below.

Previous attempts to describe the rubbery plateau in ionomers have been based on classical rubber elasticity. However, Weiss et al. found that the calculated density of network chains was lower than that calculated by assuming each pair of ionic groups forms a cross-link.[23] This discrepancy persisted even when they took into account the effect of entanglements that are trapped by the cross-links and contribute to the network. The failure of their calculation is due to the assumption that the cross-links are formed from only a pair of ionic groups. In fact, a cluster contains many ionic groups, and this higher functionality accounts for their results.

A theory for rubber elasticity which takes into account both entanglements and high functionality has been described by Pearson and Graessley.[32] Their approach allows an average cross-link functionality to be calculated from the experimental modulus and molecular parameters.

Table 4. Calculated Network Functionalities

sample	functionality at the minimum in tan δ	sample	functionality at the minimum in tan δ
2H2	2.6 ± 1.5	8H8S	10.8
5H5	2.2	2Z2S	6.3
8H10	2.1	5Z5S	2.8
2Z2	2.8	7Z8S	5.1
5Z5	2.6	2ZSPS	7.6
7Z10	7.8	5ZSPS	14.9
2H2S	5.9	7ZSPS	76.7
5H5S	5.6		

It is important to note that calculations of this type assume the use of an equilibrium modulus. For these calculations a dynamic modulus, and not an equilibrium modulus, was used. In fact, there may be no equilibrium rubbery modulus for ionomers. As a result, the calculated values for the functionality cannot be considered as absolute values, but the trends should shed some light on the nature of the ionic clusters. It should also be noted that these calculations assume that the plateau modulus is determined solely by the cross-link density and is not affected by the total polymer molecular weight. This may not be an accurate assumption, but again these calculations are intended only to illustrate the general trend in behavior for these blends.

Results of the calculation are shown in Table 4. The functionalities are calculated for temperatures at the minimum in tan δ, which is between the glass transition and the cluster transition. At these temperatures the clusters are stable and expected to act as cross-links. The ionomers show functionalities ranging from 8 to 80 as the sulfonation level is increased from 2 to 7%. These high apparent cross-link functionalities are consistent with either the MacKnight or the Eisenberg model. In both of these models there is no restriction on the size of the cluster, which acts as the effective cross-link. Connolly has used the same approach to analyze the moduli of sulfonated polystyrene ionomers and found that the average functionality is essentially infinite.[22] This result has led him to conclude that the aggregates act as reinforcing filler particles, in addition to the cross-linking effect. The difference between his results and the results presented here is due to sample preparation. The samples for this work were annealed for 6 min at the molding temperature, while Connolly's samples were annealed for 30 min. Thus the ionomers in Connolly's work probably have larger, more developed clusters. This difference illustrates the importance of consistent sample preparation when studying ionomers.

The results in Table 4 show quantitatively the effect of blending on the state of aggregation. For example, 7ZSPS has an average functionality of about 80, while the functionalities for 7Z10, 7Z8S, and 8H8S are 8, 5, and 11, respectively. (The differences among these three blends are probably insignificant). This drop in functionality will affect the modulus in the rubbery region, although the exact nature of this effect will depend on how the balance between aggregated and unaggregated ionic groups changes. If there is no change in this balance, then a drop in functionality means an increase in cross-link density, and the modulus should increase. Our data, however, show that the modulus actually decreases (see Figure 9), suggesting that there is actually an increase in the number of unaggregated ionic groups upon blending. However, it should be noted that we have not measured directly the number of aggregated and unaggregated ionic groups.

There are several explanations for why the aggregation is less in the blends, in terms of both a lower functionality and fewer aggregated ionic groups. In the case of the zinc blends it may be due to steric effects and the greater cooperativity of motion among different chains needed to form a cluster in the blends compared to ZSPS. This greater cooperativity arises because the zinc ion is coordinated to only two sulfonates in the ionomer, while it is coordinated to two sulfonates and two pyridines in the blends.[29] Thus, in the ionomer only two chains need to move to allow the ionic group to become part of a cluster, while in the blend four chains need to move. This increased difficulty in forming a cluster would lead to a reduced cluster size. In the case of the acid blends, the greater difficulty in forming a cluster may be due to both the steric effects as in the case of the zinc blends and also a reduction in mobility of the ionic groups due to the greater strength of the interactions between groups compared to the zinc-neutralized materials. These explanations are consistent with work by Moore et al., in which it was shown that aggregation increases with increasing distance of the ionic groups from the polymer backbone.[33] This result was explained as being due to more efficient packing as the ions are moved further from the bulky backbone.

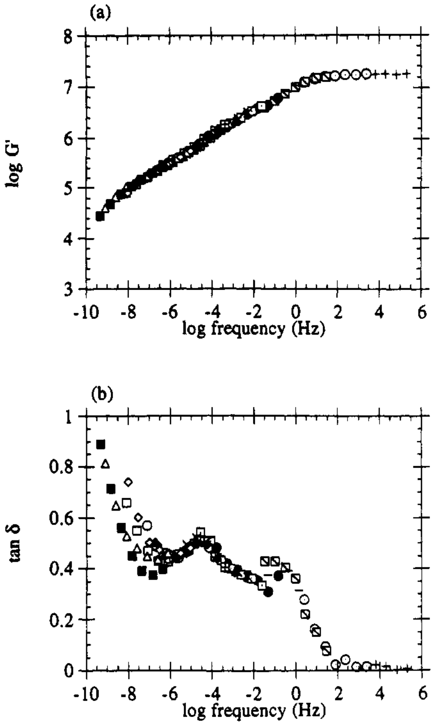

Figure 10. Master curves of (a) storage modulus and (b) tan δ for 7Z8S. Isotherms are indicated by different symbols and from high to low frequency on the master curves were measured from 120 to 260 °C intervals.

To further examine the relaxation behavior of the blends, frequency–temperature superposition was attempted for the zinc ionomers and the SPS/SVP blends. Superposition was not attempted for the blends containing ethyl acrylate to avoid the complication caused by the ethyl acrylate phase. As a check of the experimental procedure it was confirmed that polystyrene exhibits excellent superposition. The best fit WLF parameters for polystyrene from the experimental shift factors are $C_1 = 11.8$ and $C_2 = 52.5$, which is in excellent agreement with the results of Connolly ($C_1 = 9.2$, $C_2 = 51$),[22] who also used a Polymer Laboratories DMTA, and in reasonable agreement with the detailed analysis of Plazek ($C_1 = 14.5$, $C_2 = 50.4$).[34]

As an example of the failure of frequency–temperature superposition in the blends, the master curve for blend 7Z8S is shown in Figure 10. Master curves for the other

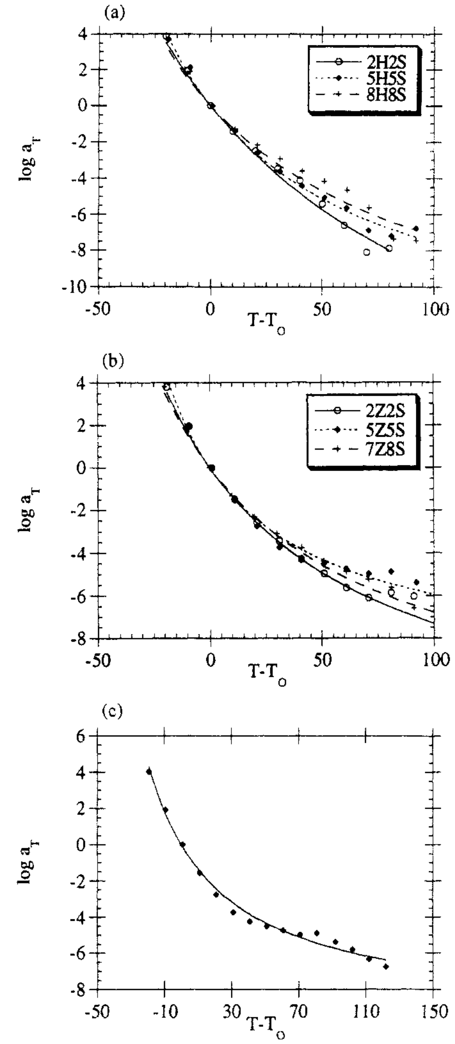

Figure 11. WLF plots for (a) acid blends and (b) zinc blends. Part c is the WLF plot for blend 5Z5S to highlight the sigmoidal nature of the data. Points are the experimentally determined shift factors. The line is a fit of the data to the WLF equation.

Table 5. WLF Constants

sample	T_0 (°C)	C_1	C_2
polystyrene	100	11.8 ± 0.5	52.5 ± 4.6
2H2S	120	23.0 ± 3.9	151.2 ± 34.4
5H5S	130	14.5 ± 1.1	91.5 ± 10.3
8H8S	140	15.4 ± 2.8	114.4 ± 30.5
2Z2S	120	14.3 ± 1.4	95.8 ± 16.3
5Z5S	130	9.6 ± 0.4	61.5 ± 4.3
7Z8S	140	13.2 ± 0.8	95.2 ± 9.8

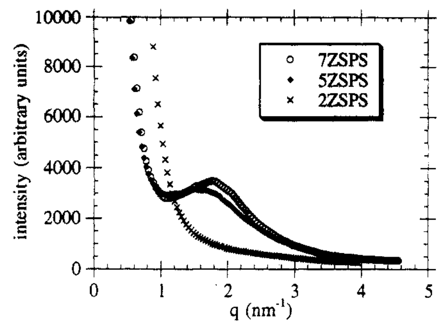

Figure 12. SAXS plots for sulfonated polystyrene zinc ionomers.

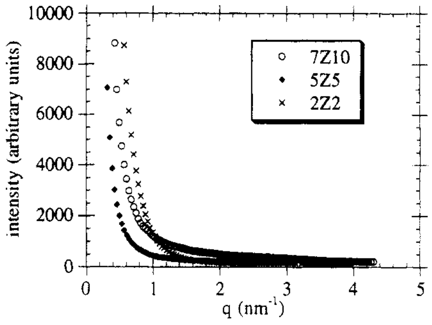

Figure 13. SAXS plots for zinc styrene/ethyl acrylate blends.

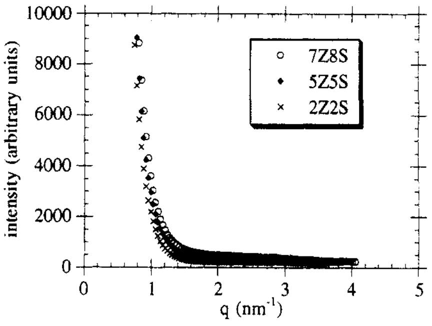

Figure 14. SAXS plots for zinc styrene/styrene blends.

blends are similar. The failure of superposition, especially at the lowest frequencies, indicates that these materials are thermorheologically complex. The shift factors are plotted in Figure 11 along with fits to the WLF equation, and the resulting WLF constants are given in Table 5. The sigmoidal shapes of the plots in Figure 11 are typical for thermorheologically complex materials. The sigmoidal shape results from the superposition of two different relaxation time distributions, each of which follows a different WLF equation.

The values of C_1 are fairly independent of the material, which is in agreement with the iso-free volume theory of the glass transition.[35] The iso-free volume theory states that the glass transition occurs when the free volume becomes so small that the large-scale cooperative motions typical of the glass transition are no longer possible. The values of C_2 are much higher than the values for polystyrene. Deriving the WLF equation from the Doolittle equation shows that C_2 is inversely proportional to the expansion coefficient of free volume (α_f).[35] The increase in C_2 represents a decrease in α_f due to the restricted mobility of the polymer chains caused by the interactions. There is no obvious trend in the effect of substitution level on C_2.

A previous study on ionomers by Connolly has found a similar increase in C_2 and failure of superposition.[22] However, Weiss et al. found that their data superposed to give a master curve that covered at least 20 decades of frequency.[23] It is not clear why superposition succeeded in their case. Nevertheless, it is evident that the failure of superposition in the ionomer blends described here confirms the presence of phase-separated ionic clusters with a distinct relaxation time distribution.

SAXS. The general features of the scattering from ionomers are a peak at intermediate scattering angles and a low-angle upturn. These features are evident in the scattering curves for the ZSPS's shown in Figure 12. As has been reported previously, the ionic peak increases in intensity and moves to slightly higher scattering angles with increasing sulfonation.[5,7] The Bragg spacings corresponding to these peaks are 37.0 and 34.9 Å for 5ZSPS and 7ZSPS, respectively. These values are similar to what has been reported previously.[5,7]

The scattering curves for the blends are shown in Figures 13 and 14. The most obvious features are that there is no ionic peak in the zinc blends, although the upturn is still present. The SAXS curves for the few samples that were not annealed for 24 h were also measured to check the gross affects of annealing. These curves also did not show the presence of an ionic peak. Although different annealing conditions will result in subtle changes in the SAXS patterns,[25] the disappearance of the ionic peak in the blends is evidently not affected to any large extent by the annealing conditions used here.

It is important to be sure that the absence of a peak in the data for the zinc blends is not a result of insufficient contrast. The electron density for polystyrene has been reported as 340 e/nm^3 and the electron density for zinc benzenesulfonate hexahydrate as 510 e/nm^3.[6] Assuming these two species represent the matrix and cluster compositions, respectively, the electron density contrast for the ionomers is 170 e/nm^3. Assuming no change in the mass density, the replacement of two of the water molecules with pyridine gives an electron density for zinc benzenesulfonate bipyridine tetrahydrate of 534 e/nm^3. Thus, the electron density contrast in the blends has actually increased by approximately 24 e/nm^3. While these are rough estimates, they do illustrate that there is sufficient contrast in the blends to detect an ionic peak if one is present.

The absence of an ionic peak in the zinc blends is due to the effect of blending. Absence of an ionic peak was also seen by MacKnight et al. in ethylene ionomers that were saturated with water.[5] In that case, the result was explained as being due to the water increasing the local dielectric constant and screening the electrostatic interactions between ionic groups, thus eliminating the depleted shell region of their core–shell model. Fitzgerald et al. have also seen a decrease in the peak intensity with the addition of methanol.[36] On the other hand, Yarusso and Cooper have found that the addition of water to sulfonated polystyrene ionomers sharpened the ionic peak,[37] and Fitzgerald and Weiss found that the addition of small amounts of glycerol substantially increased the intensity of the peak.[38] The difference is probably due to the amounts of solvent added. When only small amounts are added, the polar solvent acts to solvate the ions, resulting in a greater charge separation and a greater electrostatic driving force for aggregation. At saturation, however, the solvent increases the local dielectric constant, screening the changes and reducing the electrostatic attraction between ionic groups.

In the next section we discuss our experimental results in light of three models for ionomer morphology.

Ionomer Morphology. The data presented in this work allow for an evaluation of the three models of ionomer morphology described in the Introduction. First we consider the hard-sphere liquid-like interference model of Yarusso and Cooper.[6] In this model the clusters are arranged with a liquid-like degree of order, and the ionic peak in SAXS measurements is due to a distance of closest approach of the clusters. However, the scattering curves of the blends show that the ionic peak is not present, even though a cluster transition is present in the dynamic shear measurements. It is hard to imagine a situation in which the distance of closest approach is eliminated while still leaving the clusters intact, since it is the clusters that define that distance.

Next we consider the core–shell model.[5] As has already been mentioned, the absence of an ionic SAXS peak in ethylene ionomers saturated with water was explained as being due to an electrostatic screening effect. Under this scenario the absence of the ionic peak in the SAXS curves of the blends is due to a screening of the electrostatic interactions by the pyridine substituent. If the pyridine substituent in the blends is considered to be a diluent, it is clear that the blends fall into the category of high diluent levels, since the blends were prepared at a sulfonate/pyridine ratio of 1. In terms of the core–shell model, it would appear that the absence of the ionic peak in the blends is due to the electrostatic screening effect of pyridine, resulting from the increased charge separation between interacting groups in the blends compared to the ionomers (as described in the Viscoelasticity section). Since the pyridine substituents are attached to polymer chains, there may also be an additional effect due to the increased steric requirements and higher level of cooperativity needed to allow four polymer chains to become part of a cluster in the case of the blends, compared to the requirements for only two polymer chains, as in the case of the ionomers. The reduced level of interaction between individual multiplets results in the destruction of the preferred distance defined by the shell thickness. However, the multiplets are still intact, resulting in a high-temperature viscoelastic transition due to motion of the ionic groups. For this model we would suggest that, unlike telechelic ionomers, no interparticle interference peak is seen in random ionomers because the random placement of ionic groups along the backbone does not allow for a regular distribution of clusters throughout the material.

Finally we consider the restricted mobility model of Eisenberg et al. This model states that the "cluster" is actually a region of restricted mobility of hydrocarbon chains.[8] These chains are restricted due to the cross-linking effect of multiplets, which are small aggregates consisting of ionic groups in contact with each other. The cluster transition in this model is the glass transition of the chains with restricted mobility.

As has been described in previous sections, some of the data presented here are consistent with this model. For example, the high values of cross-link functionality are explained by the large size of the cluster regions, which act as the effective cross-links. The absence of the SAXS peak is also explained by this model. In this case, the absence of a SAXS peak is due to the breakup of larger aggregates, resulting in zinc ions being uniformly distributed throughout the material. The continued presence of the high-temperature viscoelastic loss peak is then due to regions of restricted mobility from these uniformly distributed multiplets.

However, some of the viscoelastic data appear to be inconsistent with the restricted mobility model. We consider the action of plasticizers on ionomers. In the context of the Eisenberg model the action of a polar plasticizer is to "loosen" the multiplet, allowing greater mobility for the restricted hydrocarbon chains. If this were the case, one would expect the cluster transition temperatures and activation energies to occur in the same order because the same mechanism is involved for each of them. If one plasticizer were more effective than another, then the more effective plasticizer would result in a lower transition temperature and a lower activation energy. The results described here show that this is not the case. For example, ZSPS has a higher transition temperature than the ZSPS/SVP blends, but the blends have the higher activation energy. We also note that it is unlikely that the restriction in mobility caused by ionic cross-links is sufficient to create an increase in T_g of 150 °C. Although regions of restricted mobility have been identified in networks,[39] the effects are nowhere near the magnitude that is proposed for ionomers.

Conclusions

This work has, for the first time, examined extensively the distribution of the ionic groups within ionomeric blends. Overall, the results show that the ionic groups cluster, as in ionomers, but that the size and nature of the aggregates are affected by blending. In particular, the cluster transition temperatures as measured by dynamic shear measurements are lowered for the blends compared to the ionomers. Comparison of the results for styrene/ethyl acrylate and styrene/styrene blends shows that both the pyridine substituent and the ethyl acrylate segments incorporated into the cluster act as internal plasticizers. A quantitative analysis of the dynamic shear moduli shows that the average functionality drops from 80 in the 7% zinc ionomer to approximately 5–10 for the corresponding blends. The scattering data also support the view that the effect of blending is to plasticize the clusters. The suppression of the ionic peak in SAXS measurements is the same result that has been seen for ionomers plasticized with low molecular weight compounds.

Interestingly, even though the acid forms of sulfonated polystyrene do not show a cluster transition, the corresponding acid blends do show a cluster transition. The cluster transition in the acid blends is due to the acid/base interaction between sulfonic acid and pyridine, which results in charge separation between the sulfonate anion and pyridinium cation. This charge separation provides the electrostatic interactions required for the formation of aggregates.

Activation energies for the cluster transitions occur in the order HSPS/SVP > ZSPS/SVP > ZSPS > ZSPS/EAVP. This order is rationalized on the basis of the degree of charge separation within the interactions and provides evidence that the ionic cluster transition occurs due to dissociation and motion of the ionic groups. This result supports the view that flow in ionomers occurs via an ion-hopping mechanism.

An advantage of investigating aggregation in the blends has been that the results provide insight into the morphology of ionomers. Unfortunately, the data presented here do not allow for any conclusions as to which model is most appropriate. More definitive experiments are needed for resolving the question of ionomer morphology.

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