Structure-Property Relationships of Isoprene-Sodium Styrene Sulfonate Elastomeric Ionomers

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ABSTRACT

Polymers containing less than 10 mol % of ions (ionomers) have been studied in depth for their potential in producing polymers with tailored properties for specific applications. A small molar percentage of ions can be incorporated into a polymer to drastically enhance the properties of the polymer. An ionomer that has been studied is that of isoprene copolymerized with sodium styrene sulfonate (poly(I-*co*-NaSS)). Research has been performed relating to the synthesis and chemical characterization of the copolymers. However, an in depth study of the way the physical properties are affected by a change in ion concentration has not been presented. Thus, it is the goal of this thesis to synthesize a series of poly(I-*co*-NaSS) copolymers with varying levels of sulfonated styrene and characterize their physical properties.

The poly(I-*co*-NaSS) polymers, containing a range of 1.15 to 4.74 mol % NaSS, were polymerized using free radical emulsion polymerization. The copolymer compositions were confirmed using combustion sulfur analysis. Dynamic light scattering indicated that large aggregates were present in solution. These aggregates were large enough that capillary intrinsic viscosities could not be measured. Small angle x-ray scattering (SAXS) and thermal analysis showed little change as the ion concentration was increased, while tensile, stress relaxation and adhesion properties were improved. The absence of changes in the SAXS patterns indicated that there was an absence of a

well-defined ionic aggregate, while the mechanical properties showed evidence of electrostatic interactions. This can be at least partially attributed to ionic interactions on a smaller scale (doublets, triplets).

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GENERAL AUDIENCE ABSTRACT

This research pertains to the creation of a series of polymers containing small amounts of ionic groups that allow tailoring the properties of the materials. The main component of the polymer is polyisoprene, which is also referred to as "natural rubber". This material is elastic and can be used as a rubber (gloves) or can be manipulated to create a strong adhesive through addition of ionic groups.

The polymers were synthesized with varying levels of ionic groups, creating a series of six polymers. These polymers were tested for their chemical composition (the chemical make-up of the polymers), morphological properties (their phase structure and self-assembly of the polymers on a nanometer to micron scale), and their mechanical properties (the strength, elasticity, and adhesive properties of the polymer). It was determined that in terms of the morphology, the polymer remained mostly unchanged as the ion content was increased, but the mechanical properties improved dramatically. As the concentration of ionic groups increased, the strength of the polymer as well as the adhesive properties of the polymer, also increased. Understanding the structure-property relationships of these copolymers can allow researchers to tailor their structures to fit a desired application.

Dedication

       This thesis is dedicated to my grandfather, the late Howard Hawkins, who opened his home and came out of retirement to support my family for many years. His constant love, support, and encouragement were irreplaceable.

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The friends I have made at Northstar Church are worthy of as much praise as I can type in one document. To name only a few: Dr. Rachel McCord, Dr. Jamie Sanchez, Dr. Bethany Gibson, Jenn Wilson, Julie Thompson, Erinn Briele, Charlotte Kimmel, Rebecca Lansford, Stephanie Gamble, Jamie Fillman, Dr. Jake Fillman and many more that shouldn't be left off this page, but I have only so much space to type.

To my family. Mom, you support me through thick and thin and have made so many sacrifices throughout my entire life to get me to where I am today. Aunt Susie and

Uncle Kevin, thank you for letting me do laundry at your house during undergrad and for allowing me to spend so much time with you every summer growing up. Elliot and Kara, thank you for allowing me to invade your home and play with my nephews every time I am in Oklahoma. The time I spend with you and your family is my absolute favorite. To my grandma and late grandpa, thank you for supporting my family when we had nowhere else to go. Without your help and support, I don't know where any of us would be. Last but surely not least, Maddux. Coming home to you every day has helped get me through the hardest days in graduate school. Even if you shed, and bark when someone knocks on the door, it would have been impossible to have kept my sanity without you.

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Chapter 1. Introduction and Literature Review

1.1 Motivation of research

The fundamental science of understanding how the presence of ion containing units affect the properties of a polymer has been studied in depth. The objective of this research is to further understand the effect of the concentration of ion containing units within a copolymer of isoprene and sodium styrene sulfonate. These copolymers have been previously prepared and studied.[1–4] However an investigation of ion concentration on the physical, thermal and mechanical properties has not been reported. These copolymers have potential for applications as adhesives and thermoplastic elastomers, so understanding the precise way the ionic sodium styrene sulfonate affects the behavior of the polyisoprene can yield fundamental structure-property information. Such relationships may be translated into tailoring the copolymer composition to enhance performance characteristics for specific applications.

1.2 Ionomer background

There is a continuing search to obtain new and modified polymeric materials with performance characteristics that enable specific applications.[5,6] Over the past few decades, studies have been performed focusing on the introduction of ion containing monomers into a polymer backbone which permits intra- and intermolecular ionic association in the polymer systems.[5] Ion-containing polymers, ionic polymers and ionomers are all terms that have been used to describe these polymer backbones containing pendant ionic groups. There is a distinction made between ionomers, which contain a maximum of 15-20 mol% ionic groups, and polyelectrolytes, which contain

ionic groups in higher concentrations.[7] More current studies consider only polymers with a maximum of 10 mol% ionic groups to be ionomers.[6]

One of the first notable ionomers came with invention of Surlyn® at DuPont in the 1960s.[8] Surlyn is a copolymer of ethylene and methacrylic acid containing an ionic linkage with either a univalent or divalent cation. The structure modified low density polyethylene to have high strength and good clarity.[9] Rees, who discovered what would become Surlyn®, noticed that in solution experiments, a "gel-like" material formed and he found that it was due to the pendant ionic groups and their ability to interact and form ion-rich aggregates in a nonpolar matrix.[8,10] A schematic of ionic aggregates is shown in Figure 1.1. This aggregation is critical to the polymer properties. These properties depend on numerous aspects of the chemistry of the polymer including the type of backbone, ionic content, type of attached (fixed) ion, degree of neutralization and the type of counter cation or anion. All of these variables are what make this such a broad area of research.[10] Theoretical models have been proposed to explain the way the ions aggregate and how this aggregation affects phase separation within the polymer.
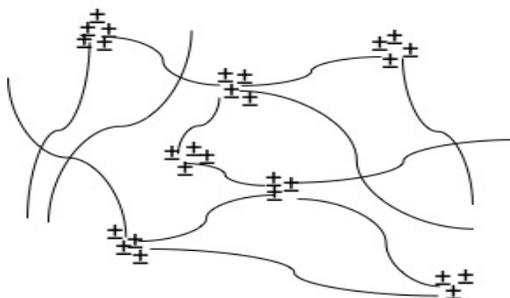
Figure 1.1 Schematic of ionic aggregates with + being a metal ion and – being the anion on the polymer backbone. The lines are hydrocarbon chains with no ions attached.

Two of the commonly studied ions used to create ionomers are pendant carboxylate and sulfonate ions. Lundberg and Makowski[11] used polystyrene as the polymer backbone to compare these two anions with sodium ions as the counterion. They found that sulfonate ionomers "possess much stronger ionic associations than corresponding carboxylates" as well as the finding that this association persists at higher temperatures. They suggest that this is due to the higher degree of polarity found in the sulfonate ionomer when compared to the carboxylate ionomer.

1.2.1 Elastomeric ionomers

Tant and Wilkes[12] reviewed some of the properties that make a polymer an elastomer. It has the ability to be stretched and return to its original dimensions. The modulus required to elongate the material is low compared to glassy polymers. Weak secondary bonding is exhibited in the majority of the systems in the solid state, which will form a network structure (this is necessary for the recovery to the polymer's original dimensions upon load removal) among other things.

There are many examples of elastomeric ionomers. The first ionomer discovered, Surlyn, was in fact an elastomeric ionomer.[10] The incorporation of ions into the rubber matrix of elastomers can lead to altered physical properties such as enhancing the "rubbery plateau" similar to that of linear segmented elastomers. This is attributed to associations of ionic aggregates that function as crosslinks.[4] Thermoplastic elastomers are a subset of elastomeric ionomers. These ionomers are elastomers that have a high degree of ionic association. A subset of this class of materials has a sufficiently reduced degree of ionic association at processing temperatures to permit adequate melt flow

processing.[13] One well-studied thermoplastic elastomer is comprised of a poly(ethylene-propylene-diene) monomer terpolymer (EPDM). A pendant ionic group can be attached, creating an elastomeric ionomer. This will be further considered in this review.

1.2.2 A common elastomeric ionomer: Poly(Ethylene-propylene-diene) monomer (EPDM) terpolymers

Cross-linked EPDM is a common elastomer because of its resistance to aging due to heat, light, oxygen and ozone. This can be largely attributed to the low levels of unsaturation in these elastomers relative to polybutadiene or polyisoprene.[14,15] Figure 1.2 shows the structure of EPDM with ethylidene norbornene as the diene component. The double bond enables EPDM to cross-link, giving the polymer its elastic behavior. Another factor affecting the behavior of the EPDM terpolymer is the different levels of the three monomers in the copolymer.[16] Obviously, the diene will affect the properties as well.
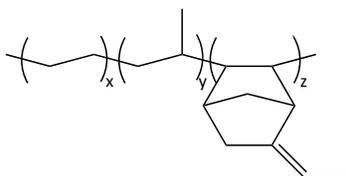
Figure 1.2. Chemical Structure of EPDM

One popular application for EPDM is as a roofing membrane due to its great durability, water barrier properties and low temperature properties,[17] as well as its advantages in flexibility and long term weathering resistance.[18] However, while the elastomer itself has great properties, one downfall is its lack of cohesion to itself or to adhesives that have sufficient peel strength to resist short and long term debonding forces.[18] A means for improving adhesion of EPDM is to sulfonate the unsaturated

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diene in the elastomer, and this also substantially improves the physical properties.[6] Carboxylating the EPDM has been studied as well, but it was found that due to the stronger ionic interactions of the sulfonate it would require lower levels in the elastomer, in comparison to the carboxylate option, to observe the desired physical property changes.[13]

1.3. Synthesis and chemical characterization of polymers

The physical and mechanical properties of a polymer always begin with the chemistry. The chemical structure, which depends on the monomer/comonomer composition and can also be dependent on the synthesis process, will directly affect the polymer properties. Aqueous emulsion polymerization is the targeted synthesis method in the research described herein.

1.3.1 Emulsion polymerization

Emulsion polymerizations can be used to create a polymer with a high yield and high molecular molecular weight.[19] These polymerizations consist of several components, including the monomer, a water-soluble initiator, surfactant (sometimes referred to as an emulsifier) and water, as the continuous phase.[8] Chain transfer agents are often added to control molecular weights.[20,21] The surfactant is important in that it stabilizes the colloidal system, preventing coalescence of the large latex particles in the solvent that would decrease their surface energy.[21]

One mechanism for emulsion polymerizations is free radical polymerization. It involves three main steps including initiation, propagation and termination, as shown in Figure 1.3 (where I is the initiator, R* is the initiator radical, M is the monomer, P is the

polymer and k_i is the rate constant for the reaction). The termination step can occur by either disproportionation or chain coupling. Disproportionation occcurs by abstraction of a hydrogen by the radical with consequent elimination on one of the components to produce a terminal double bond. This can involve the monomer, polymer, initiator, solvent, etc. or by adding a chain transfer agent specifically for this purpose. Coupling is shown as termination method "a" in Figure 1.3, while disproportionation is method "b".

Initiation	Propagation	Termination
$I \xrightarrow{k_d} 2R^*$	$P_1^* + M \xrightarrow{k_p} P_2^*$	$P_m^* + P_n^* \xrightarrow{k_{tc}} P_{m+n}^*$ (a)
$R^* + M \xrightarrow{k_i} P_1^*$	$P_2^* + M \xrightarrow{k_p} P_3^*$	$P_m^* + P_n^* \xrightarrow{k_{td}} P_m + P_n$ (b)
	$P_n^* + M \xrightarrow{k_p} P_{n+1}^*$	
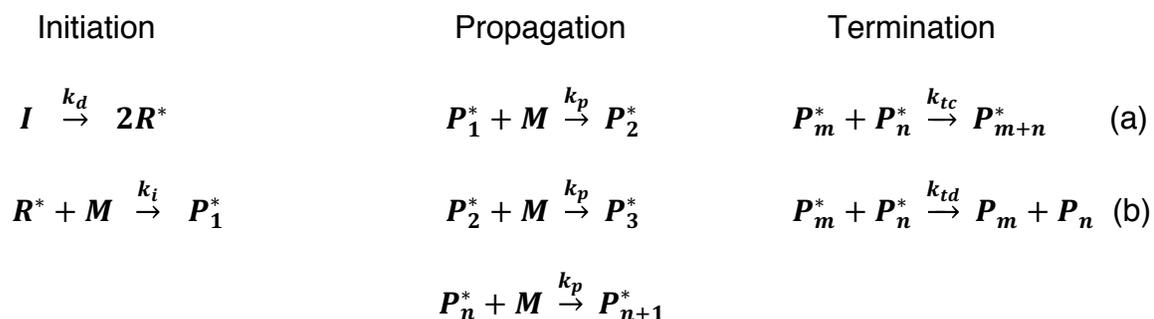
Figure 1.3. Steps of free radical polymerization[8,21]

The emulsion is stabilized by the surfactant, which is a molecule containing a hydrophilic head and hydrophobic tail. The surfactant forms a dynamic equilibrium between micelles and free single chains in solution once the critical micelle concentration (CMC) is reached. There will be large monomer droplets in the reaction system and due to the vigorous stirring required for this type of reaction, the monomers become dispersed into the surfactant micelles, where the polymer can begin to grow. In these micelles the monomer and water-soluble initiator meet and begin the polymerization. It is also possible for the initiator to meet the monomer in the aqueous phase. Termination of the reaction is controlled by the rate at which radicals from the aqueous phase since termination is bimolecular. A general emulsion polymerization schematic is shown in Figure 1.4.[8]
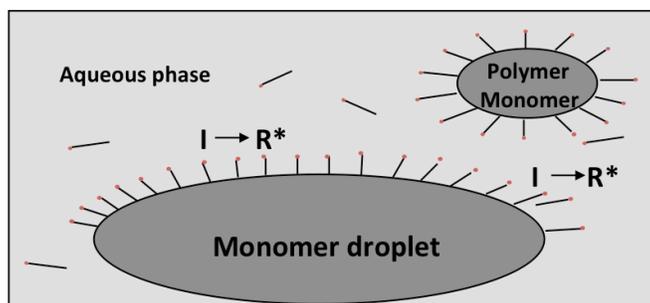
Figure 1.4 Emulsion polymerization

1.3.2 Synthesis of copolymers

A statistical copolymer consists of at least two different monomers polymerized together to achieve a mixture of the properties of the two homopolymers. Copolymers can be randomly sequenced (also called statistical), alternating, block, or graft copolymers. The different arrangements depend on the synthetic technique and polymerization conditions utilized.[8] There are numerous synthesis methods and conditions used to create these copolymers, but for this review emulsion free radical copolymerization will be the main focus.

1.3.2.1 Free radical copolymerization

In free radical copolymerization the initiation, propagation and termination steps are similar to those encountered in homopolymerizations, except that the rate constants (k) depend on whether the growing polymer chain is reacting with the monomer of the same composition at the end of the growing chain (homopropagation), or with the monomer of different composition (cross-propagation). These rate constants are depicted as k_{11}, k_{12}, k_{21} and k_{22} with the first number in the subscript representing the monomer on the end on the growing chain and the second number being that of the monomer that it is adding to it.[22] Rate constants can be used to determine reactivity

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ratios, which give indications of the propensity for the growing polymer chain to add its own monomer species or the other monomer in the copolymerization. The reactivity ratios are shown in Equation 1.1. If $r_1 > 1$ then the growing polymer chain will be more likely to add a monomer of its own species onto the end, as opposed to the other monomer species.[8] Equation 1.2 shows the copolymerization equation, which can also be referred to as the copolymer composition equation, and shows the molar ratio between the two monomer units based on the concentration of each monomer.[23]

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

Equation 1.1 Definitions for monomer reactivity ratios present for free radical

copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])}$$

Equation 1.2 Copolymerization Equation

1.3.2.2 Synthesis of ionic copolymers

Typical ionomers comprise of up to around 10 mole % of ionic groups.[6] They are comprised of non-ionic, hydrophobic monomers (with some exceptions) that contain a small percentage of ion containing units.[24] The ions on the polymer backbone can be either randomly or regularly distributed and generally they can be synthesized by either copolymerization of ionic monomers or by the chemical modification of ionogenic polymers, which are polymers that have the propensity to be ionically modified.[7]

1.3.2.3 Isoprene-sodium styrene sulfonate copolymerization

A main focus of this thesis is related to the synthesis and characterizations of a poly(isoprene-sodium styrene sulfonate), poly(I-*co*-NaSS), ionic copolymer. Figure 1.5 shows the basic reaction involved in synthesizing these copolymers.
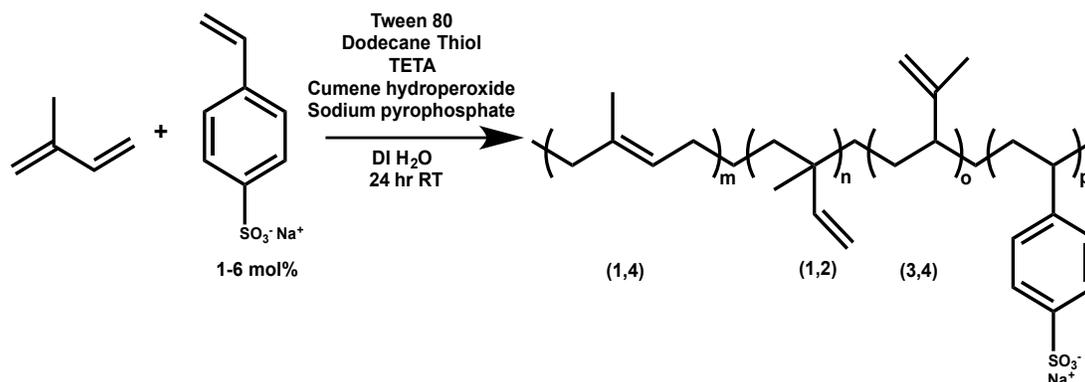
Figure 1.5 Reaction of isoprene and sulfonated polystyrene[25,26]

The synthesis of poly(I-*co*-NaSS) has been studied in numerous publications.[1–4] From these different studies two different methods have been discussed for the way the isoprene and NaSS orient themselves within the copolymer.

Turner et al.[27] studied the polymerization of styrene and NaSS and suggested a mechanism for the initiation of the free radical polymerization. A similar mechanism can be suggested for that of isoprene and NaSS. It was suggested that, since the NaSS was in the aqueous phase (having the polar sulfonate fixed ions), that it could be initiated by an initiator that was also in the aqueous phase. The NaSS would start polymerizing with other NaSS molecules, thus creating oligomers of NaSS in the water. These hydrophilic oligomers would then react with the styrene that was in small concentrations in the aqueous phase in the early stages of polymerization, then these would quickly aggregate to form stabilized particles. Juang and Kreiger[28] found similar tendencies

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that also promote this mechanism in their study of emulsifier-free emulsion polymerizations.

Siadat et al.[4] discussed a different mechanism related to the formation of these copolymers. Using a nonionic surfactant to test the mechanism they proposed that NaSS could be absorbed into a micelle where they would react with isoprene monomers to form ionic aggregates inside the micelle. The authors included a schematic of their proposed mechanism and it is shown in Figure 1.6. The manner in which the two monomers copolymerize can greatly affect the physical properties of the elastomeric ionomer.
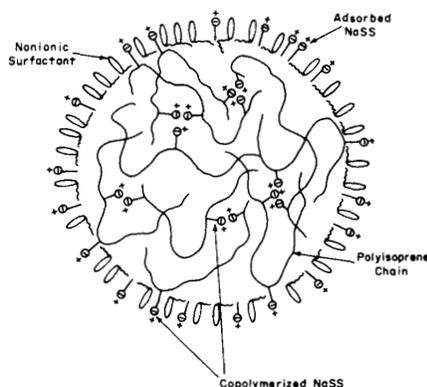
Figure 1.6 Schematic by Siadat et al. showing a micelle of a poly(isoprene-sodium styrene sulfonate) copolymer during emulsion polymerization.

1.3.3 Chemical characterization of poly(isoprene-sodium styrene sulfonate) copolymers

Siadat et al.[3,4] conducted extensive research on the chemical characterization of hydrocarbon monomers copolymerized with sodium styrene sulfonate. Their work provides a great deal of insight into both the infrared spectra and solubilities of these elastomeric copolymers.

1.3.3.1 Infrared spectroscopy of poly(I-*co*-NaSS)

Determination of the NaSS content via a spectroscopic technique has been found to be rather difficult. Thus, elemental sulfur analysis has been utilized in this research to determine and confirm compositions. Another method for determining this amount was shown by Siadat and Lenz,[3] where they found a linear relationship between the IR absorbances of isoprene and the S=O stretching peak. Thus they could determine the ratio of sulfonate groups and methyl groups in the copolymer by using Equation 1.4.

$$\frac{A_{1176}}{A_{1445}} = 10.0 \frac{C_{S=O}}{C_{CH_3}}$$

Equation 1.4[a] Relationship between the intensity of the isoprene methyl group and sulfonate S=O peak in IR spectra.[3]

1.3.3.2 Solubility of poly(isoprene-sodium styrene sulfonate) copolymer

Siadat et al.[3,4,29] tested the solubilities of the copolymers that were prepared in the emulsion copolymerizations. It was found that a hydrocarbon solvent such as toluene or xylene was sufficient to dissolve the polyisoprene homopolymer. However, due to the ionic crosslinking that was observed upon addition of the sodium styrene sulfonate, methanol was required in solvent mixtures at approximately 5% by volume. The methanol solvated the sulfonate groups and disrupted the ionic crosslinks that inhibited the the copolymers from dissolving in only the hydrocarbon solvents.[29]

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[a] Where A is the absorbance and C is the mole fraction. The authors used a baseline method to determine the intensity of the reference beams. The 10.0 in the equation represents the ratio of the extinction coefficients of the 1176 and 1445 absorption bands.[3]

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1.4. Structural and physical attributes of copolymers and ionomers

There is an influence of pendant ionic groups on the mechanical properties of ionomers.[30] Certain time-dependent properties, including creep, dynamic mechanical response and stress-relaxation, are sensitive to the strength of the ionic associations, which themselves are dependent upon the specific ion in the chain and its metal cation.[12]

1.4.1 Phase behavior of copolymers

Copolymerization of vinyl monomers can yield random (also called statistical), alternating, block, or graft copolymers depending on the polymerization methods and/or conditions used for synthesis.[8] Since it has been proposed that sodium styrene sulfonate will form as small blocks in the isoprene backbone, it is important to briefly discuss the behavior of block copolymers, before looking at ionomers specifically.

One factor that greatly affects the blending of two different monomers is their typical inability to mix together and form miscible blends. The majority of polymers are immiscible and the homopolymers will phase separate. While entropy favors mixing, the high molecular weights of polymers renders the entropy of mixing small and this usually leads to immiscibility. There are also energetic interactions between the species that can inhibit mixing.[31] A way to mix together chemically different polymers is by the formation of block copolymers. With these block copolymers there will still be some phase separation that will be most significantly determined by the covalent bond that is restricting the macrophase separation of the different blocks.[32] However, if there is a strong repulsion between the two sequences of copolymers there will be a microphase

separation. When this separation occurs the microdomains may form a regular arrangement which will form a periodic structure.[33] This will greatly affect the way the polymer behaves especially as the temperature or other processing conditions are adjusted.

1.4.2 Types of ionomers

Ionomers are typically polymers with small to modest percentages of ion containing units. These can be the result of copolymerization or can be formed during post-polymerization reactions. Figure 1.7 shows typical copolymer structures specific to ionomers, including random, telechelic, block and segmented ionomers. Random ionomers constitute a seemingly infinite range of materials that can be synthesized.[34] Being so prevalent, they are commonly studied and the morphological considerations for these random ionomers will be considered in more depth in the next section, along with segmented ionomers. Telechelic ionomers are a type of polymer that contain one ionic group at each end of the polymer chain.[12] Both monochelics and telechelics tend to show similar behavior to that of block ionomers. In other words, they differ in behavior from the more widely studied random ionomers. The morphological behavior of telechelics depends quite heavily on the molecular weights of the systems. At lower molecular weights there is a greater amount of ionic cross-linking, as there is a higher concentration of ions per chain. However, once the molecular weight increases, there is less evidence of this cross-linking, since the longer chains consequently create a lower concentration of ions in the polymer.[34]

Some Types of Ionomers

Random Telechelic Block Segmented
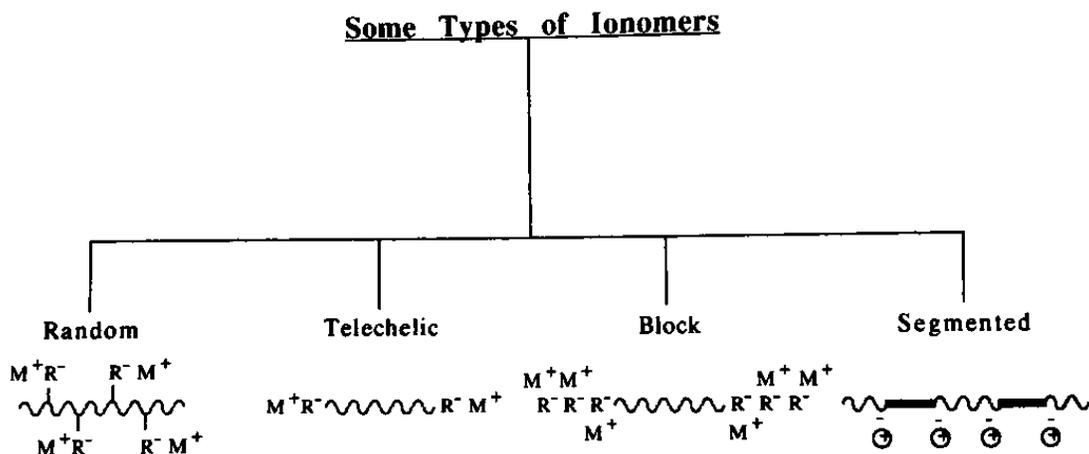
Figure 1.7 Types of ionomer structures.

1.4.3 Ionomer morphology

Since the time Eisenberg published the original theory in 1970, many models have been developed to discuss the microphase separation in ionomers.[35] Three models will be presented including the original theory presented by Eisenberg, a clustering model by Forsman that was developed in 1982, and a multiplet cluster model presented by Eisenberg et al. in 1990. One thing to be noted is that the characterization tools and subsequent analytical results related to the field have become much more sophisticated since 1970 when Eisenberg published his original model, hence the constant revisiting of the topic.

1.4.3.1 Original model presented by Eisenberg

In 1970 Eisenberg set out to create a theoretical model regarding the ways ions cluster in ionomers.[36] In this theory he sought to show that clustering is favored at high concentrations of ions and that a critical concentration had to exist. Below this point it would be energetically unfavorable for clusters to form. Also, he wanted to propose a

correlation between the size of the ion cluster, the distance between these clusters, and the effects it would have on various chain parameters.

Eisenberg theorized that there would be constraints that would affect the ions becoming multiplets (defined as "associated pairs, triplets, quartets, etc, in which the charges are as close to each other as physically possible"). He described these as 1) the dimensions of the polymer chains and the ion pairs, 2) the tension on the polymer chains resulting from aggregation of the ions if certain pairs that are nearest each other on the polymer chain become incorporated into different multiplets, and 3) the electrostatic energy that would be released upon the formation of multiplets.

In terms of the multiplet size and their separation, Eisenberg noted that the larger the ionic multiplets were with constant ion concentration on the backbone, the further apart they must be from each other and that they should be distributed randomly throughout the material. He went on to state make the assumption that the multiplet was represented as a spherical liquid drop containing only ions, while the hydrocarbon chains were segregated to only the surface of the drop, and that there was thus a well-defined phase separation.

Some factors that affect the computation of the electrostatic interactions and elastic work in ionomers are that, 1) once the cluster forms there is work done to stretch the polymer chains, 2) electrostatic energy is released when clusters are formed from multiplets, 3) the cluster is not infinitely stable and will decompose at a temperature of T_c in which the elastic forces and the electrostatic forces balance each other, and lastly 4) it is assumed that half of the sequential ion pairs (the ones closest to each other on

the chain) associated within the same cluster will form a ring. These assumptions led to Equation 1.5, to represent the number of ion pairs in an ion cluster and Equation 1.6 shows the average distance between the clusters.

$$n_{cl} = \frac{\rho N_A}{M_c}\left[l^2\frac{\overline{h^2}}{\overline{h_o^2}}\frac{M_c}{M_o}\frac{k'e^2}{3kT_cK\pi\varepsilon_o r} + 2\left(\frac{n_o M_c}{\rho N_A}\right)^{\frac{2}{3}}\right]^{\frac{3}{2}}$$

Equation 1.5[b] The number of ion pairs within a stable ion cluster as presented by

Eisenberg[35,36]

$$R_o = \sqrt[3]{n_{cl}M_c/(\rho N_A)}$$

Equation 1.6. The average intercluster separation distance[35,36]

Mauritz[35] indicated some fundamental assumptions that were made in this model. These included 1) the basis of the model on purely random coils is likely an oversimplification and the sections of the chains between ionic groups are too short to be treated in terms of Gaussian statistics; 2) crystallinity, which has the propensity to be rather significant even for low ionic comonomer mole fractions, isn't included in the model; and lastly 3) Eisenberg himself described a new model, which will be shown in section 1.4.3.3, that incorporates a region of restricted chain mobility in the vicinity of multiplets, which isn't present in his original model.

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[b] Where n_{cl} is the number of fundamental ion pairs within a stable cluster, ρ is the polymer density, M_c is the average molecular weight between ionic units, l is the length of the C-C bond, M_c/M_o is the average number of C-C bonds between ionic unites, e is the electronic charge, k is Boltzmann's constant, K is the dielectric constant of the organic medium, ε_o is the permittivity of free space, r is the center-to-center spacing of positive and negative charges in a contact ion pair, N_A is Avogadro's number, $\frac{\overline{h^2}}{\overline{h_o^2}}$ is the ratio of the mean-square end-to-end distance for the polymer chain, and k' is the fraction of electrostatic energy released upon formation of an ion pair.

1.4.3.2 Segment-segment association by Forsman

     Forsman also published a model regarding ionic effects on chain dimensions of ionomers.[37] His aim was to provide a statistical mechanical treatment of the effect that segment-segment associations would have on the dimensions of polymer molecules. For this model he made four assumptions; 1) interacting repeat units were evenly spaced along the polymer backbone, 2) Gaussian statistics not only applied to entire molecules, but also to subchains connecting the interacting groups, 3) every cluster contained the same number of repeat units and 4) every cluster was formed from only the repeat units that would be the m nearest neighbors in the absence of cluster formation. In other words, m could then be defined as the number of repeat units per cluster.[35]

     Segment-segment association will cause a decrease in the entropy of the system. Forsman describes this loss in entropy, ΔS_a in terms of a disaggregation process and defines this variable in Equation 1.7. This loss of entropy is associated with the increase in ordering of the segments into uniform dimers, trimers, etc. To devise a term for energy interactions, Forsman describes cases for both spherical (Equation 1.8) and lamellar (Equation 1.9) geometries. He then was able to devise a theoretical model for the value of m, or again, the number of repeat units per cluster, which is shown in Equation 1.10. An original goal of this model was to interpret small-angle neutron scattering and from the experimentally observed results, this model was strongly supported as being accurate.[38]

$$\Delta S_a = \frac{RCf}{M_o}\left[\frac{m-1}{m} \ln\left(\frac{C\bar{v}f}{m}\right) - \frac{(m-1)+\ln m}{m}\right]$$

Equation 1.7[c] The loss of entropy due to a disaggregation process

$$\frac{\Delta E}{RT} = -mN_c\left[\theta_1^s \frac{\theta_2^s}{m^{\frac{1}{3}}}\right]$$

Equation 1.8[d] Energy interactions in the spherical geometry

$$\frac{\Delta E}{RT} = -mN_c\left[\theta_1^1 \frac{\theta_2^1}{m^{\frac{1}{2}}}\right]$$

Equation 1.9[c] Energy interactions in the lamellar geometry

$$m^{\frac{1}{2}} = \frac{\theta_2}{4A}\left[1 + \left(1 - \frac{16A(1-\ln C\bar{v}f)}{\theta_2^2}\right)^{\frac{1}{2}}\right]$$

Equation 1.10[e] Most probable value of m

1.4.3.3 Multiplet cluster model by Eisenberg, Hird and Moore

In 1990 Eisenberg, Hird and Moore published a new model for ionic aggregation and cluster behavior in ionomers.[39] Their objective in creating this model was to incorporate the results of dynamic mechanical and X-ray scattering studies that were more recent (at the time of publication) and unavailable for previous models. There are many points in the model that follow the original Eisenberg model (discussed in section 1.4.3.1), but there are others that are expanded upon or changed completely.

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[c] Where R is the ideal gas constant, C is the polymer concentration, f is the fraction of repeat units involved in clusters, M_o is the molecular weight of a repeat unit and $\bar{v}$ is the specific volume of the polymer.
[d] Where ΔE is the total energy of interaction within a cluster of m sites, N_c is the number of clusters/volume, θ_1^s, θ_1^1, θ_2^s, and θ_2^1 are dimensionless energies that reflect the total strength of bulk and surface interactions.[35]
[e] Where $A = (\alpha^4 - \alpha^2 + 1)/\alpha^2$

In terms of the terminology used in the new model, a multiplet is still defined as an aggregate consisting of several ion pairs and only containing ionic material, and the most important parameter that affects the formation of multiplets is the electrostatic interactions between ion pairs. If these interactions aren't strong enough to overcome the elastic forces of the chains, then a multiplet will not form. An important factor in this model is the "firmness" with which the ion pairs are held in the multiplet, and that is also governed by the strength of the electrostatic interactions. In each multiplet, every ion pair will hold the polymer chain at the point of its attachment, making the polymer less mobile in the immediate vicinity of the multiplet. The further away you get from the multiplet, the more mobile the polymer will become and the stronger the electrostatic interactions in the multiplet, while closer to the multiplet the more rigid they become and the more they restrict the mobility of the polymer. The authors provided a schematic of this region of restricted mobility around a multiplet, and it is depicted in Figure 1.8. The distance at which the mobility is restricted is thought to be in close relation to that of the polymer persistence length, also defined as a length of the polymer chain in which only short range intrachain effects are present.[35]
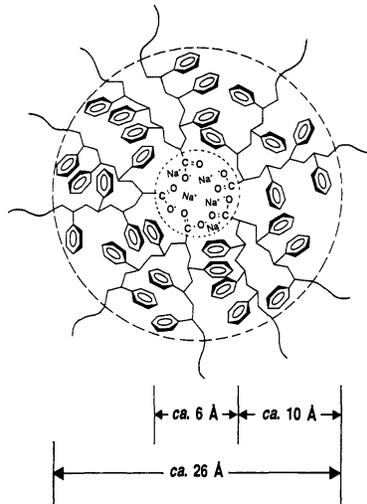
Figure 1.8 Schematic of the region of restricted mobility surrounding a multiplet in an ionomer.

Eisenberg et al. turned to the nature of multiplets and their relation to ion clusters in a polymer. As the concentration of ions was increased the distance between the multiplets began to decrease and their regions of restricted mobility began to overlap. As the number of overlaps increased, they increase in size, and a much larger region of restricted mobility forms - large enough to have its own glass transition temperature (T_g). This region was then referred to as a cluster and exhibited the properties of a microphase-separated region. In these cluster regions, there was no thermodynamic driving force for phase separation. It was based solely on the restricted mobility of the chains due to the ionic multiplets that caused the clustering. These clusters exhibited well-defined mechanical characteristics that clearly demonstrated phase-separated behavior.

The authors used small angle X-ray scattering (SAXS) and dynamic mechanical analysis to confirm the model validity. The specific details of their testing are beyond

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the scope of this review, but it is important to note that the results of the experimentation did in fact corroborate the predictions in the model.

1.5 Potential application as an adhesive

1.5.1 Basics of adhesion

The definition of an adhesive is a material that binds two things (can be referred to as adherends) together. Chemical properties tend to dictate how an adhesive binds between two surfaces, as the chemical structure and properties control the mechanical properties between the adhesive and the surface.[40]

There are several classes of polymeric adhesives including water based emulsion systems, solvent based, reactive and hot melt systems.[1] While all of these types of adhesive formulations are successful commercially, current environmental standards push for the production of these adhesives to be more environmentally friendly,[2] in particular, eliminating toxic and/or air polluting solvents.

1.5.2 Ionomers as adhesives

Due to their ability to wet a surface quickly while resisting detachment make ionomers well suited as pressure sensitive adhesives.[41] Over the years, specifically in the 1980s, there have been an abundance of patents claiming the use of ionomers as adhesives (Agarwal et al.,[1,2,42–44] Fieldhouse[18,45] and Bartman[46]). A common theme in these patents is that the molecular weight and ionic content, not unexpectedly, play a huge role in the properties of the adhesive, and they must be properly balanced to optimize the performance of the polymer.[41]

1.5.3 Neoprene as an adhesive for EPDM
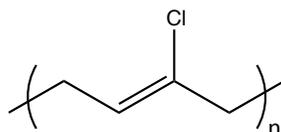
Figure 1.9 The chemical structure of neoprene

Neoprene, or poly(chloroprene), while not an ionomer, is a commonly used adhesive to bind rubber and a number of chloroprene adhesives have been created.[47] The structure of neoprene is shown in Figure 1.9. The reason for its common use is that it exhibits excellent initial adhesive strength and it has superior properties with numerous adherends.[47] Neoprene adhesives typically show excellent resistance to creep and cold flow.[48] However, there are many reasons to avoid neoprene in industrial uses. The most detrimental property of neoprene adhesives is the need to use environmentally unfriendly solvents, such as aromatic (xylene) and others that pose health hazards, environmental concerns and flammability concerns.[49] For these reasons, an adhesive that has similar favorable adhesive properties, but without the solvent health concerns, is a desirable goal for adhesive development.

1.5.4. Poly(Isoprene-sodium styrene sulfonate) as a rubber adhesive

In the 1980s, isoprene copolymerized with sodium styrene sulfonate became documented and patented as a promising copolymer for adhesive applications.[2,43,44,50] While it showed promising features, the neoprene-based systems are still in use today. Due to a recent upsurge in American federal regulations regarding the use of harmful solvents (such as those used with neoprene adhesives), it is of great interest in

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industrial applications to find an adhesive system based on less harmful solvents, while also showing the required adhesive properties.

1.6 Proposed work: characterization and structure-property relationship of polyisoprene ionomers

This review will conclude by discussing the research plan to take an in depth look at poly(isoprene-sodium styrene sulfonate) ionomers. This will be advantageous in discovering the fundamental structure-property relationships of the ionomer as the ion concentration is systematically changed. There are multiple ways that the chemistry of this ionomer can be changed, including changing the positive counterion from sodium to an alternative,[51–55] altering the percentage of the styrene sulfonates,[3,4,19,27,29,52,56,57] changing the anion from a sulfonate to a different ion, such as a carboxylate,[11,52,54,55,58] or modifying the polymer backbone by adding styrene monomer that does not have a pendant ionic group. From these additions, the glass transition temperatures (T_gs) can be intentionally changed[59] and other physical properties can be tested to observe how they react to this change. The focus of the work will be on observing the property changes when altering the level of sodium styrene sulfonate in the ionomer.

1.6.1 Structural characterization

To determine the chemical composition, several experimental methods can be used including Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), elemental analysis, solubility tests, titration methods and molecular weight determinations. FTIR and NMR are used to quantify specific functional groups in the polymer. The peaks that are observed in the FTIR spectra for poly(I-co-NaSS) are

those that were outlined by Siadat et al.[3] in section 1.3.3.1. NMR is a very useful technique, but the previously mentioned (section 1.3.3.2) solubility issues a drawback for using NMR to study poly(I-co-NaSS). This copolymer requires a nonpolar solvent to dissolve the isoprene, mixed with a polar solvent to disrupt the ionic associations.[29] It could be possible to use co-solvents when running an NMR experiment and for this polymer deuterated toluene and deuterated methanol can be used. However, one thing to note is that the peak for deuterated toluene aligns with the peak for NaSS, making the data qualitative, not quantitative.

1.6.2 Physical characterization

A method for determining the molecular weight of an ion-containing polymer is by measuring the instrinsic viscosity of the polymer. The Mark-Houwink-Sakurada equation, Equation 1.11, depicts the relationship between molecular weight and the intrinsic viscosity. The viscosity of a fluid is defined as the resistance to flow of the fluid.[8] One way to measure viscosity is to dissolve the polymer and time the solution as it runs through a capillary viscometer. If done using a series of different concentrations, the inherent and relative viscosities can be extrapolated to zero, giving the intrinsic viscosity. The equations for these different types of viscosity measurements are shown in chapter two.

$$[\eta] = KM^a$$

Equation 1.11[f] The Mark-Houwink-Sakurada equation relating intrinsic viscosity to molecular weight.[8]

In terms of the mechanical properties of the polymer, there are several tests that can be run. Tensile tests can be conducted to measure the amount of stress that is required to yield and break the polymer. Dynamic mechanical anaylsis (DMA) can be used to measure the molecular relaxation properties of the polymer on a time and temperature dependent basis. Melt rheology can be utilized to determine the melt flow properties of the polymer, such as viscosity of the polymer melt, melt flow at specific shear rates, etc., and viscoelasticity tests such as creep, which shows how much of a load is required to deform the polymer.

One of the best tools to determine a polymer morphology is small angle X-ray scattering (SAXS). This technique is powerful for morphological determination of ionomers due to the 10 Å to 100 Å ideal length scale that can be measured with this technique. This scale coincides with the scattering from crystalline lamellae and other microphase separated systems.[61] SAXS functions by impinging an X-ray beam into the polymer film that will cause several diffraction rings to appear, providing the user with a great deal of information about the polymer structure. The rings are created when the X-ray beam diffracts from the polymer at specific angles at different intensities.[8]

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[f] Where $[\eta]$ is the intrinsic viscosity, K and a are constants that are characteristic to the polymer in question, and M is the molecular weight.

1.6.3 Thermal characterization

There are several techniques that can test the thermal stability of polymers, and these can then provide insight to some of the basic properties of that polymer. One of these is thermogravimetric analysis (TGA) that determines the weight loss as a function of temperature or time, and that can provide information regarding polymer degradation as a function of temperature. Another method of thermal testing is differential scanning calorimetry (DSC). This method is used to heat the sample and measure the amount of heat given off or taken in by the system. One can determine the glass transition temperature(s) (T_g) and crystalline transitions of a polymer. DMA can be used wih varying frequency and temperature to determine molecular relaxation behavior of the polymer. This will inform the user of the behavior of the polymer as the temperature is changed.[8] As previously mentioned, the chemistry of the polymer can be changed to intentionally alter the T_g of the system,[59] so thermal testing will be an integral piece to measure this change.

1.6.4 Adhesion Testing

Since one of the objectives of this research is to study the properties of the ionomer in question as a rubber adhesive, testing the adhesive strength of the polymer has been performed. One property to be tested when investigating a potential adhesive is the contact angle that the adhesive has with the adherend. Contact angle measurements allow one to observe the wettability of a polymer, or the propensity of aliquid to spread on the surface.[62]

Once it has been determined whether or not the prospective adhesive can properly wet the surface of the adherend, then the mechanical testing of the adhesive can commence. Two basic measurements to determine the strength of an adhesive are the peel test and the lap shear test. The peel test is used to measure the strength of an adhesive joint, to ensure that adequate bond strength exists in the adhesively bonded structure.[40] The peel test involves coating the desired adherend with the adhesive and measuring the amount of force that is required to peel samples apart. This force is related to the properties of the interface between the adhesive and the adherend, and it can be a direct measure of interfacial toughness.[63] The lap shear test, also referred to as a tensile-shear test, is used to measure the strength of the adhesive as it is sheared, as opposed to being pulled apart as in the peel test. Two adhesive-coated samples will coat the adherend while a force is applied to both pieces until fracturing of the sample occurs.[40]

1.7. Conclusion

Elastomeric ionomers are a specific class of polymer with properties that can be easily manipulated and tailored for applications as thermoplastic elastomers or adhesives. In the following chapters, the process and data will be shown, regarding how to create an elastomeric ionomer with isoprene and approximately 1-5 mol % of sodium styrene sulfonate. These copolymers were synthesized using free radical emulsion copolymerization. Different ion concentrations were incorporated to further the knowledge of how this type of elastomer will behave through this fundamental modification. A number of analytical techniques were employed to determine the

chemical and physical characteristics of the ionomer. Some of these included TGA, DSC, DMA, tensile testing, SAXS, and peel tests, among others. The goal of this research is to understand the fundamental behavior of an isoprene polymer that has been copolymerized with sodium styrene sulfonate, and how such materials can be modified to deliver the best physical properties possible for the desired application.

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Chapter 2. Effect of Ion Concentration on the Properties of Polyisoprene-Sodium Styrene Sulfonate Elastomeric Ionomers Prepared by Emulsion Polymerization

2.1 Abstract

A series of polyisoprene-*co*-sodium styrene sulfonate (poly(I-*co*-NaSS)) were synthesized with systematically varied concentrations of ions using free radical emulsion polymerization. Their chemical structures and morphologies were characterized and structure-mechanical relationships were determined. While the SAXS and thermal properties remained unchanged as ion content increased, the stress-strain, stress relaxation and adhesion properties were significantly improved as the ion content increased from 1.15 mol % to 4.74 mol % NaSS.

2.2 Introduction

Ion containing polymers introduce intra- and intermolecular, non-covalent bonding into a polymer system. Through the manipulation of the nature of the ions and the polymer backbone, scientists can tailor the properties of the polymer for use in specific applications.[1] Two ionomer functional groups that are commonly utilized are metal sulfonates and metal carboxylates attached to the polymer backbone via a styrene unit. It has been shown that sulfonate ionomers allow much stronger ionic associations than carboxylate ionomers,[2] thus creating a more pronounced effect on the polymer properties. Ionomers can be used in many applications including adhesives, thermoplastic elastomers, rheology modifiers, etc.[3] Polymers containing low levels (< 10%) of ionic groups can exhibit properties that are dominated by the intra and intermolecular, noncovalent interactions of the ionic groups.

A system of isoprene copolymerized with low molar percentages of sodium styrene sulfonate (poly(I-*co*-NaSS)) has been investigated.[4–9] These previous investigations focused on the emulsion copolymerization of isoprene with sodium styrene sulfonate,[4–7] for use as a pressure sensitive adhesive,[8] and as a viscosity modifying agent in drilling fluids.[9] The focus of all of these previous studies was an investigation of the polymerization of the poly(I-*co*-NaSS) and chemical characterization of the resulting materials. The solubilities of poly(I-*co*-NaSS) was also investigated.[10]

A series of poly(I-*co*-NaSS) with systematically varied amounts of sodium styrene sulfonate ionomers was prepared in this study. The structure-property behavior regarding morphological, thermal and mechanical properties as the ion content was changed are reported in this manuscript. Poly(I-*co*-NaSS) has the potential for applications as an adhesive or as a thermoplastic elastomer. Understanding the manner in which the ionic sodium styrene sulfonate units affect the behavior of the polyisoprene can yield fundamental structure-property information which may be translated into tailoring the copolymer composition to enhance performance characteristics for specific applications.

2.3 Experimental

2.3.1 Materials

Sodium styrene sulfonate, cumene hydroperoxide, triethylenetetramine (TETA), Tween 80, 1-dodecanethiol, hydroquinone and 2,6-di-*t*-butyl-4-methyl phenol (DBMP) were purchased from Sigma Aldrich and used as received. Isoprene was obtained from

Sigma Aldrich with tert-butyl catechol as an inhibitor. The monomer was stored at 5 °C, and prior to polymerization it was washed three times in a separatory funnel with 0.5 M NaOH followed by three washes with distilled water to eliminate the inhibitor.[4] After the washings, the isoprene was distilled at atmospheric pressure. Care was taken to have the final product collected in a flask partially submerged in an ice bath to avoid loss of isoprene, due to its high volatility. The sample was then sealed with a rubber stopper and purged with argon for 5 min, again, with the flask partially submerged in an ice bath. The purified isoprene was either used immediately or stored at 5 °C until needed.

2.3.2 Synthesis of poly(I-*co*-NaSS)

An emulsion polymerization method presented by Siadat et al.[5], was adapted to prepare the poly(I-*co*-NaSS) series of polymers. Sodium pyrophosphate (0.3 g, 3.36 x 10^{-4} mol) and the desired amount of sodium styrene sulfonate (NaSS) (1.0 g, 2.42 mmol) were added to a 250-mL round bottom flask and capped with a rubber septum. Sixty mL of deaerated distilled water and TETA (0.5 g, 1.68 x 10^{-3} mol) were charged to the same flask via syringe, followed by a five-minute purge of argon gas. Into a separate 100-mL flask, Tween 80 (3.5 g, 1.31 x 10^{-3} mol), 14% dodecanethiol in toluene (0.43 g, 1.47 x 10^{-4} mol dodecanethiol) and cumene hydroperoxide (0.51 g, 1.68 x 10^{-3} mol) were added, and the flask was capped with a rubber septum. Isoprene (34.1 g, 0.25 mol) was added to the flask via syringe. The material from the 100-mL flask was then added to the 250-mL flask via syringe while running a purge of argon to maintain a constant pressure. The flask was placed in a water bath at room temperature and stirred for 22 h. A solution of 6 mL of methanol containing 0.048 g hydroquinone and 0.1

g DBMP was added to the flask and allowed to stir for 10 min. The milky white material was then transferred into 500 mL of methanol where it immediately began to coagulate. The solution was stirred for 24 h before being filtered with a Büchner funnel. The solid was added to 500 mL of DI water and stirred for 24 h before filtration. The polymer was dried overnight under vacuum at 50 °C. Once removal from the oven the polymer was wrapped in foil, purged with argon and stored in the dark to prevent any photo-induced cross-linking. When the polymers were needed for testing, they were taken out of the jar, then immediately returned to the dark storage area.

2.3.3 Characterization

2.3.3.1 Chemical

A Varian FTIR with a PIKE GladiATR attachment was used for infrared spectroscopy of the samples. The S=O stretching peak[5] at approximately 1200 cm^{-1} qualitatively shows the sulfur level in each polymer. To quantitatively determine the sulfur levels in each polymer elemental analysis was conducted using combustion analysis performed by Atlantic Microlab Inc. DLS was utilized to confirm ionic aggregation. All polymer samples were dissolved at a concentration of 0.1 wt% polymer in solvent. The solvent for polymers with concentrations of NaSS lower than 3.0 mol % was 95/5 v/v% toluene/1-butanol, while for polymers with concentrations of NaSS higher than 3.0 mol % was 90/10 v/v% toluene/methanol. The individual samples were sonicated in a glass vial for 1 min in a Branson 5800 Sonicator at 20 °C. The samples were then withdrawn using a glass syringe equipped with an 18-gauge needle and transferred through a 0.20 μm PTFE syringe filter to a quartz cuvette. The cuvette was

then placed into the Malvern Zetasizer Nano Series DLS which measured the particle diameter of the samples at 25 °C. There was a 30 second equilibration time before three measurements were taken. Each measurement was the average of 10 scans that were each 10 seconds long. Intrinsic viscosity was measured using a Cannon-Fenske size 75 viscometer at 25 °C. A single polymer was measured in solution at five different concentrations (0.10, 0.25, 0.50, 0.75, and 1.0 g/dL). The inherent and reduced viscosities were plotted and the intrinsic viscosity was determined from the viscosity at zero concentration.

2.3.3.2 Film preparation

The solvents used for the preparation of films were the same as mentioned for DLS testing in the previous section. A solution of 5 wt% polymer in solvent was stirred overnight at room temperature. The viscous fluid was then poured into a polystyrene Petri dish containing a polytetrafluoroethylene (PTFE) liner (Welch Fluorocarbon). The film was allowed to air dry in a vent hood for 24 h, then dried in a vacuum oven at 50 °C overnight. This method produced a film of approximately 0.5 mm in thickness.

2.3.3.3 Thermal

TGA was performed on a TA Q500 instrument using nitrogen as the purge gas, with a starting temperature at 25 °C and increasing at a rate of 10 °C/min up to 600 °C. DSC tests were performed using a TA Q1000 DSC with nitrogen as the purge gas. The procedure utilized a "heat-cool-heat" series of cycles that involved heating from -80 °C to 190 °C at 5 °C/min, quench cooling back to -80 °C, then heating to 190 °C at 5 °C/min.

2.3.3.4 X-Ray Scattering

Small angle x-ray scattering (SAXS) measurements were conducted using a Rigaku S-Max 3000 3 Pinhole SAXS system equipped with a rotating anode emitting x-rays with a wavelength of 0.154 nm (Cu K-α). The sample to detector distance was 1600 mm, and the q-range was calibrated using a silver behenate standard. Two dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 2 h. All SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated SAXS intensity versus scattering vector q, where q=(4pi/λ)sinθ, θ is one half of the scattering angle and λ is the wavelength of the x-ray.

2.3.3.5 Mechanical

DMA temperature ramp experiments were performed using a TA Q800 DMA at a frequency of 1 Hz and a temperature ramp from -105 °C to 150 °C at 2 °C/min cooled with liquid nitrogen. Due to the affinity of polyisoprene to thermally cross-link at high temperatures, the ramp was not taken higher than 150 °C. To measure the stress/strain behavior and hysteresis, films were cut into dogbones measuring 32 mm x 2 mm x 0.5 mm (length x width x thickness). Tensile measurements were made at a strain rate of 30 mm/min on an Instron 5500R. To measure hysteresis, the same Instron was utilized and the samples were stretched to between 30-50% strain depending on the tensile properties of the polymer. Stress relaxation tests were performed using 10 mm long samples on a TA Q800 DMA at 40 °C. The samples were taken to a strain of 50% and the stress relaxation was monitored for 1 h after deformation. Hysteresis was

determined for each polymer film. The films were cut into dogbones with the previously mentioned dimensions. Each polymer was taken to the maximum % strain achievable while still remaining in the initial linear region of the stress/strain curve (these strain percentages will be shown in the results and discussion section). The strain rate for all samples was 30 mm/min. Once the maximum strain was achieved, the polymer was relaxed at a rate of 30 mm/min to zero percent strain. One elongation (loading) and relaxation (unloading) counted as a cycle, and five cycles were performed. The percent hysteresis was calculated by taking the ratio of the area bounded by the loading-unloading curves to the total area under the loading curve.[11]

2.3.3.6 Adhesion

Samples were dissolved in 15 wt % solution (concentrations of NaSS lower than 3.0 mol % used 95/5 v/v% toluene/1-butanol, while for polymers with concentrations of NaSS higher than 3.0 mol %, 90/10 v/v% toluene/methanol was used), doctor bladed at a thickness of 50 μm and a width of 1 in (24 mm) onto a sheet of mylar, then dried overnight under vacuum at 50 °C. The samples were adhered to steel plates by placing the adhesive side onto the plate and rolling a steel roller of approximately 2000 g over the Mylar twice. A 180° peel test was performed using a ChemInstruments Adhesion/Release Tester AR-1000 and pulled at a rate of 5 mm/s.

2.4 Results and discussion

2.4.1 Polymer Structure

The chemical structures of the poly(I-*co*-NaSS) copolymers were characterized by infrared spectroscopy, combustion elemental analysis, intrinsic viscosity and

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dynamic light scattering (DLS). Nuclear magnetic resonance (NMR) spectroscopy did not yield quantitative results, likely due to differences in solubilities of polymers with high ion contents that led to incomplete dissolution. Figure 1 shows the qualitative IR results. As the charged mol % of NaSS was increased, the S=O bond absorbance at (1200 cm^{-1})[12] increased as expected. To quantitatively confirm the amount of NaSS in the copolymer, combustion sulfur analysis was performed and the results are shown in Table 1. The error for this technique is only approximately ± 0.3 % of the measured value, and this allows accurate determination of the comonomer content even at the low concentrations that were investigated. The data clearly confirm that the incorporated levels of NaSS increased as the feed concentration of NaSS increased.
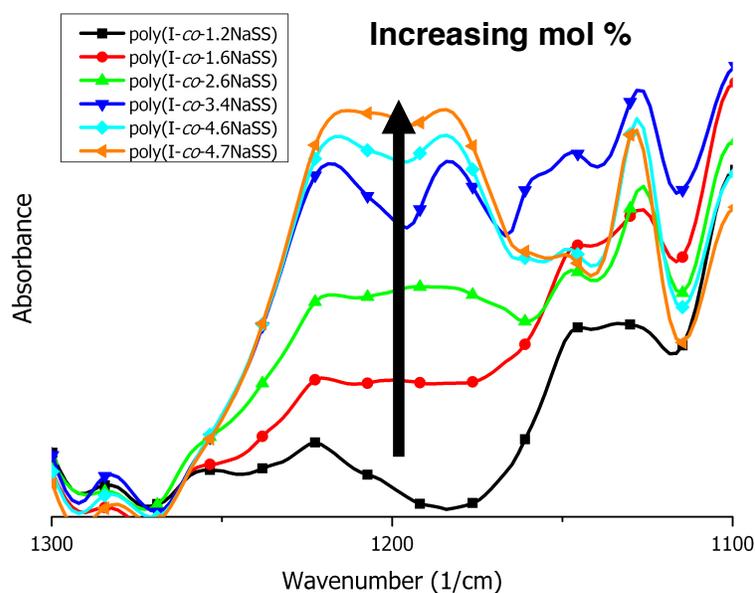

Figure 2.1 FTIR S=O stretching for poly(I-*co*-NaSS) containing varied amounts of NaSS

Copolymers	Theoretical mol % NaSS	Theoretical weight % sulfur	Measured weight % sulfur	Measured mol % NaSS
poly(I-co-1.2NaSS)	0.96	0.15	0.18	1.2
poly(I-co-1.6NaSS)	1.9	0.30	0.25	1.6
poly(I-co-2.6NaSS)	2.8	0.44	0.41	2.6
poly(I-co-3.4NaSS)	3.9	0.61	0.53	3.4
poly(I-co-4.6NaSS)	4.6	0.72	0.73	4.6
poly(I-co-4.7NaSS)	5.5	0.87	0.75	4.7

Table 2.1 Compositions of a series of poly(I-co-NaSS) with increasing concentrations of NaSS obtained from elemental analysis

Molecular weights were estimated from intrinsic viscosities that were measured in mixed solvents in an attempt optimize dissolution of the ionic and nonpolar components. Size exclusion chromatography could not be utilized due to aggregates that were present in the solution as confirmed by dynamic light scattering (DLS). To determine the molecular weight by intrinsic viscosity measurements, the Mark-Houwink-Sakurada (MKS) equation was utilized[13] where $[\eta]$ is the intrinsic viscosity, K and α are the MKS parameters measured in toluene and M_v is the viscosity molecular weight:

$$[\eta] = KM_v^{\alpha}$$

Homopolymerized polyisoprene can contain several different stereochemistries including cis-1,4-, trans-1,4-, 1,2-, and 3,4-polyisoprene, with each isomer leading to different K and α values. Free radical emulsion polymerized polyisoprene has a distribution of isomers as follows: 24.4% cis-1,4, 62.0% trans-1,4, 6.1% 1,2, and 7.5% 3,4.[14] K and α values have been measured for 100% trans-1,4-poyisoprene[13] and for 70% cis-1,4, 23% trans-1,4 and 7% 3,4-polyisoprene.[15] The viscosity results for the copolymers with lower amounts of NaSS are shown in Table 2, utilizing the K and α

values from references 14 and 15. Notably all of the molecular weights were high, in the range of 200,000 to 300,000 g/mol. The copolymers containing above 3.0 mol % of NaSS aggregated significantly and could not be measured.

Copolymers	Intrinsic viscosity (dl/g)	Approximate Molecular Weight (M_v) (g/mol)[a]	Approximate Molecular Weight (M_v) (g/mol)[b]
poly(I-*co*-1.2NaSS)	1.29	197,000	172,000
poly(I-*co*-1.6NaSS)	1.50	242,000	211,000
poly(I-*co*-2.6NaSS)	2.05	371,000	322,000
poly(I-*co*-3.4NaSS) poly(I-*co*-4.6NaSS) poly(I-*co*-4.7NaSS)	Samples swelled and would not go through the capillary viscometer		

Table 2.2 Intrinsic viscosity and approximate molecular weights for poly(I-*co*-NaSS) polymers. (a)[13] uses K and α values of 1.76×10^{-4} dl/g and 0.73 for 100% trans-1,4-polyisoprene, and (b)[15] using K and α values of 1.72×10^{-4} dl/g and 0.74 for 70% cis-1,4, 23% trans-1,4 and 7% 3,4-polyisoprene.

DLS was used to probe the aggregate structures of the copolymers. The polymers containing 1.2 mol % and 1.6 mol % of NaSS flowed easily through the filter. However, all of the other polymers that were tested contained aggregates that compromised the filtration. For the two polymers that were successfully filtered, the correlation data showed evidence of large aggregates with high polydispersity. The DLS results for both polymers were multimodal, thus supporting the aggregated structures that could be attributed to either chemical crosslinking or high molecular weight.

2.4.2 Morphology

SAXS provides information about polymer systems based on the differences in electron density within the system. In ionomers, there are two domains with different electron densities, the ionic domains and the nonpolar domains. Ionomers containing randomly distributed ionic groups tend to have decreased contrast between the ionic

and nonpolar domains due to unordered distribution of electron density.[16] Copolymers of styrene and sodium styrene sulfonate have been shown to contain small blocks of 3 to 4 NaSS repeat units randomly distributed throughout the hydrocarbon backbone so a low contrast is expected for this polymer.[17] Typically, the characteristic ionomer peak lies at q values in the range of 1.5 – 2.5 nm^{-1}.[18,19] Figure 2 shows the scattering curves obtained from SAXS for the series of poly(I-*co*-NaSS) polymers. The scattering profile for poly(I-*co*-1.2NaSS) is featureless and does not suggest the presence of well-ordered ionic aggregation. Although deviation in the scattering curves in the vicinity of 0.5 q is present in the higher ion-content polymers, these shoulders are broad and likely due to diffuse aggregation of ionic groups. Unlike typical polystyrene based ionomers there is no evidence of large-scale aggregation or of a well-defined multiplet structure.
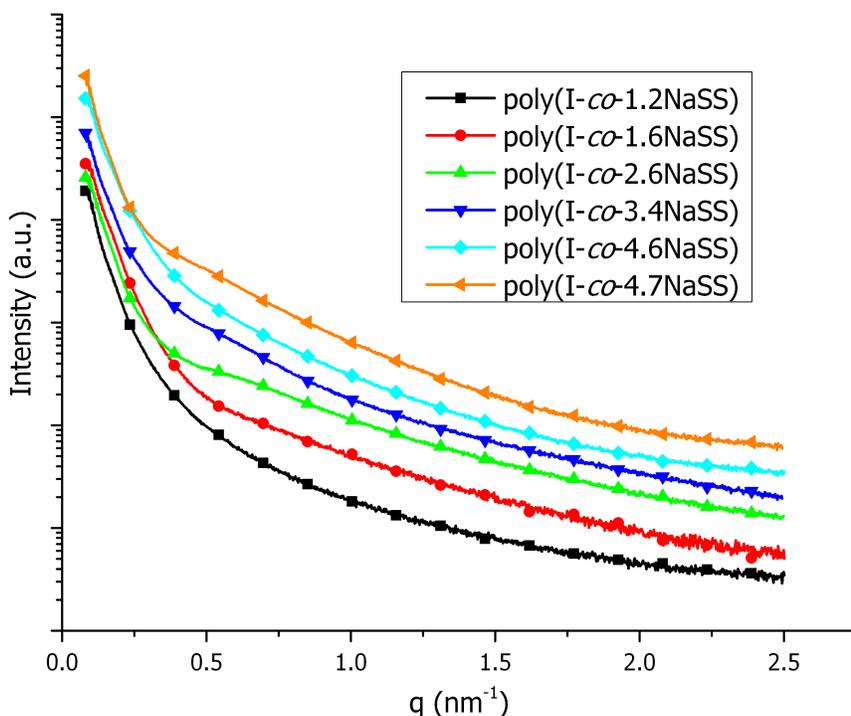

Figure 2.2 Vertically shifted SAXS results for poly(I-*co*-NaSS) samples

Copolymer	5% weight loss (°C)	T_g (°C)	tan delta (°C)
poly(I-*co*-1.2NaSS)	341	-62.1	-42.1
poly(I-*co*-1.6NaSS)	339	-60.8	-41.1
poly(I-*co*-2.6NaSS)	336	-61.7	-41.1
poly(I-*co*-3.4NaSS)	322	-60.7	-41.2
poly(I-*co*-4.6NaSS)	330	-61.1	-41.4
poly(I-*co*-4.7NaSS)	325	-60.9	-41.1

Table 2.3 Temperature at 5 % weight loss determined by TGA, T_g determined by DSC, and tan delta determined by DMA

The thermal properties of the polymers were tested to better understand the morphological changes as ion concentration increases. Table 3 shows that the glass transition temperatures (T_g) measured by both DSC and DMA are not changed as the ion content changes. It is reasonable to assume that the copolymers with low concentrations of ions may not significantly affect the T_g. However, at higher concentrations of ions the relatively unchanged T_g suggests that the ions could be aggregated in a separate phase. If there was presence of well-defined ionic aggregation, a systematic shift in the T_g would be expected.

One thing that is certain from the T_g results is the confirmation of the polyisoprene isomer present. The T_g of cis-1,4-polyisoprene is approximately -73 °C, while the T_g of trans-1,4-polyisoprene is -58 °C as measured by differential scanning calorimetry (DSC).[20] This confirms that the polymers contain more of the trans-1,4 isomer as the T_g is close to the -58 °C (as measured by DSC) value found in the literature. Also of note is the fact that the DMA tan delta value is approximately 20 °C higher than the T_g measured by DSC. It is not uncommon for the DMA T_g results to be higher than those measured by DSC, due to the differing testing methods (e.g.

measuring frequency instead of heat flow).[21] It has been found that when performing free radical homopolymerization of polyisoprene the isomer compositions in the polymers are 24.4 % cis-1,4, 62.0% trans-1,4, 6.1% 1,2, and 7.5% 3,4.[14,22] Since the copolymerization of isoprene and sodium styrene sulfonate is a free radical polymerization, it is reasonable to expect the levels of isomers in the isoprene portion of the polymer to be similar to previously measured homopolymer values.

2.4.3 Mechanical properties

The storage moduli of the polymers are shown in Figure 3. All six polymers are rubbery at -105 °C. After the decrease in moduli, all of the polymers show a plateau indicating the inability to flow. This inability to flow again indicates a potential for chemical crosslinking in the polymers. The plateau height increases as the concentration of ions increase, which indicates an increase in stiffness, and potentially and increase in the concentration of crosslinks.
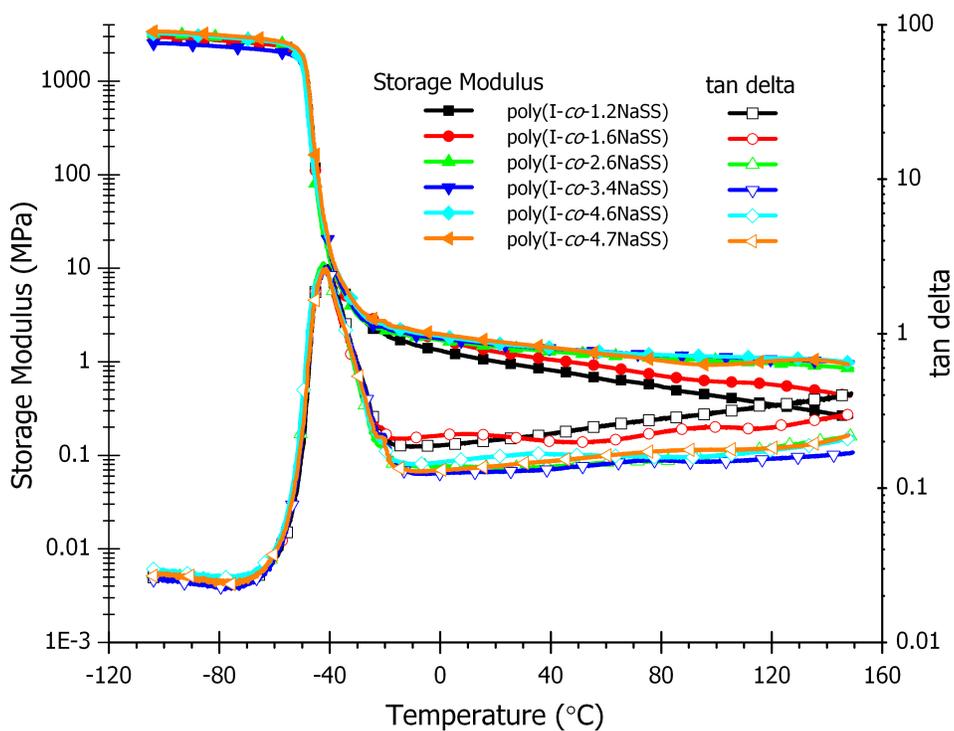
Figure 2.3 Storage moduli from DMA for a series of poly(I-*co*-NaSS)

Figure 4 shows the stress-strain behavior of the poly(I-*co*-NaSS) polymers. With an increase in NaSS, the stress and strain at break increase substantially. The three copolymers with the least amount of ions have weak mechanical properties, but the three copolymers containing the higher concentrations of ions are stronger. While the scattering profiles and the thermal behavior indicate little evidence of large-scale aggregation, the tensile traces are consistent with small-scale electrostatic interactions. This data suggests the presence of ionic doublets and triplets interacting within the polymer.
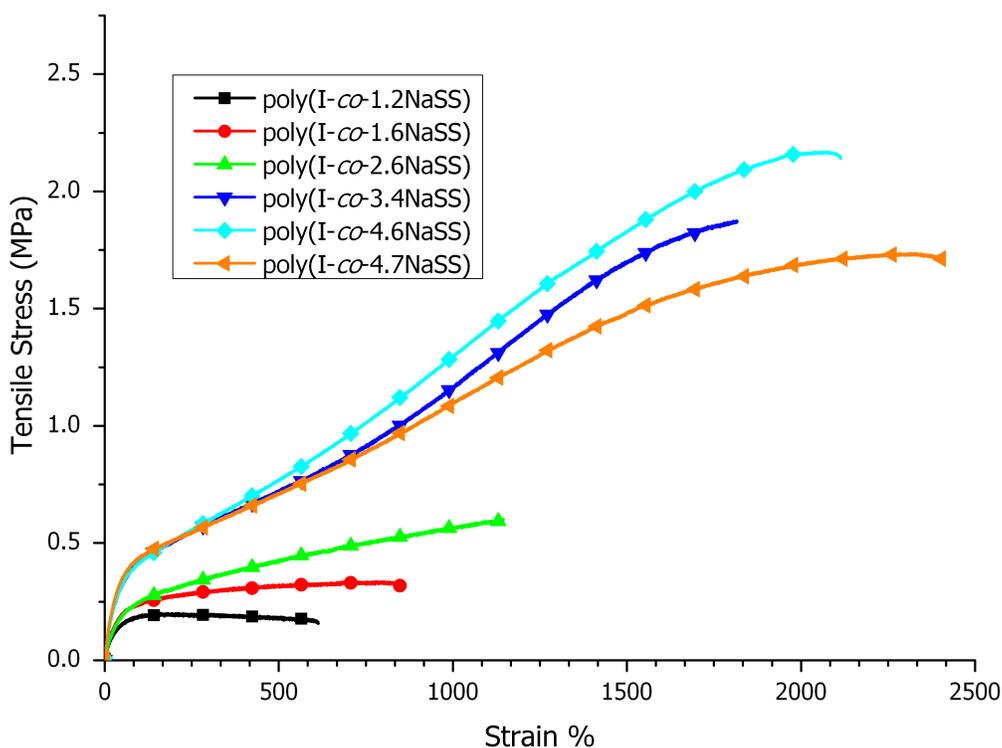
Figure 2.4 Stress vs strain behavior for a series of poly(I-*co*-NaSS) samples

The stress relaxation results (Figure 5) show that as the ion concentration increases, the copolymers can maintain a higher stress over time at 50 % strain. Poly(I-*co*-1.2NaSS) and poly(I-*co*-1.6NaSS) show a large reduction in stress. This confirms the stress-strain behavior. As the ion concentration increases, the strength of the polymer also increases. The poly(I-*co*-1.2NaSS) and poly(I-*co*-1.6NaSS) samples are unable to maintain the stress level exhibited by the other four polymers.
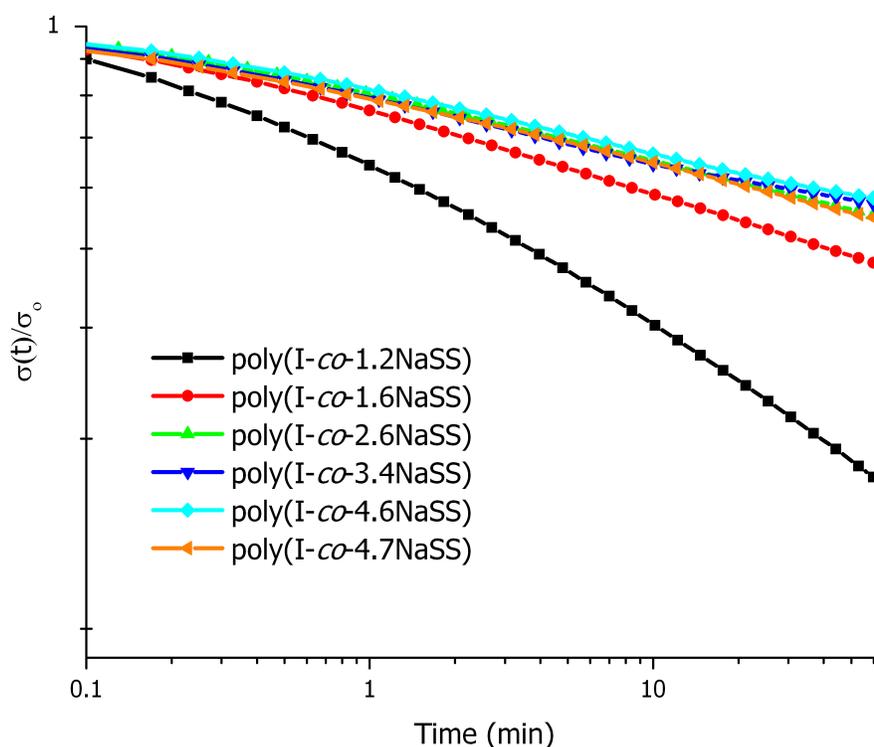
Figure 2.5 Stress relaxation behavior for a series of poly(I-*co*-NaSS) samples

Although well defined, large-scale ionic aggregation was largely absent in the SAXS scattering profiles, the tensile and stress-relaxation data suggest that small-scale electrostatic interactions are responsible for the mechanical properties of the poly(I-*co*-NaSS) copolymers. Small ionic doublets and triplets contributing to the electrostatic physical cross-links are the likely result of the established relationship between the distribution of NaSS repeat units and the polymerization method for this particular system as presented by Turner et al.[17] During the emulsion polymerization, the NaSS monomer is present in the aqueous phase, while the isoprene monomer is in a separate, nonaqueous phase. Upon initiation, the NaSS will begin polymerizing with other NaSS monomers in the aqueous phase prior to introduction into the non-aqueous phase and subsequent co-polymerization with the isoprene monomers. This leads to

small blocks of randomly distributed NaSS throughout the isoprene backbone. With the evidence of chemical cross-linking confirmed by DLS and viscosity measurements, the small blocks of NaSS would be restricted within the cross-linked network, preventing large-scale aggregation of the ions. This would confirm the presence of doublets and triplets suggested by the tensile and stress-relaxation results, while also explaining the absence of a characteristic ionic aggregate peak in the SAXS scattering profiles.

The percent hysteresis was measured for each polymer at the strains shown in Table 4, where the stress-strain properties were in the linear region. In terms of the percent hysteresis, all of the copolymers were within approximately 7 % of each other. There was evidence of a slight decrease in percent hysteresis as the ion concentration increases, with a slight increase in percent hysteresis for the two polymers with the highest ion concentration. This indicates that the ion concentration does not have much of an impact on the initial increase in strain and recovery from that strain. This is likely due to the fact that the network hasn't been sufficiently altered to allow the ions to come into contact with each other. Future work should include testing the hysteresis at higher strains.

Copolymer	Maximum strain (%)	% Hysteresis First Cycle	Avg. % Hysteresis Second-Fifth Cycles
poly(I-*co*-1.2NaSS)	25	29.0	27.8 ± 0.4
poly(I-*co*-1.6NaSS)	30	25.5	23.8 ± 0.3
poly(I-*co*-2.6NaSS)	30	23.0	21.2 ± 0.2
poly(I-*co*-3.4NaSS)	40	21.7	19.2 ± 0.1
poly(I-*co*-4.6NaSS)	40	24.6	22.2 ± 0.2
poly(I-*co*-4.7NaSS)	45	26.5	23.4 ± 0.4

Table 2.4 Hysteresis results for poly(I-*co*-NaSS) copolymers

2.4.4 Adhesion peel testing

The adhesion of the copolymers to steel was measured in 180° peel tests. As the ion concentration increased the peel strength generally increased significantly, due to the increase in adhesive strength created by the electrostatic interactions within the polymer. One anomaly appears to be the peel strength decreases in the poly(I-*co*-4.7NaSS) copolymer. It is not clear why this is the case.
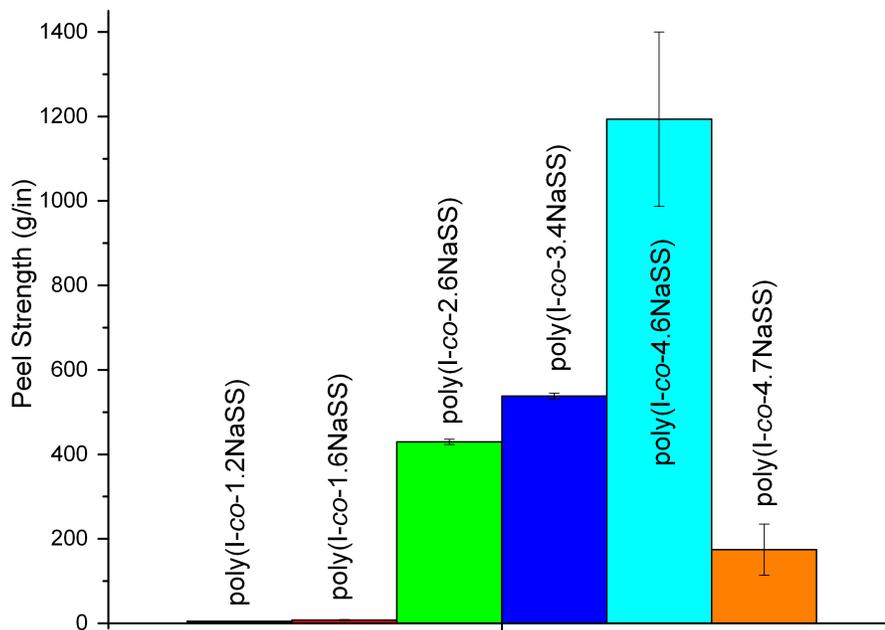

Figure 2.6 180° Peel Test data for poly(I-*co*-NaSS) samples

2.5 Conclusions

As the ion concentration increases in the poly(I-*co*-NaSS) copolymers, both the SAXS results and the thermal properties indicate chemical crosslinking. Moreover, the cross-linked network prevents the ions within the copolymer from aggregating. However, once stretched, the ions can interact with one another, significantly increasing the mechanical properties of these polymers. This is manifested uniformly in the tensile,

stress relaxation and adhesion properties. This study provides fundamental interrelationships among chemical structure, morphology and physical behavior.

2.6 Acknowledgements

2.7 Chapter two references

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2.8 Chapter two supplemental information

2.8.1 Synthesis of poly (I-*co*-NaSS) using a thermal initiator

Chemical	Purpose	Amount (mol)	Amount (g)
Water	Aqueous phase	2.22	31.0
Isoprene	Monomer	0.250	17.0
Sodium styrene sulfonate	Ionic comonomer	0.00242-0.0121	0.5-2.5
Potassium persulfate	Thermal initiator	7.4×10^{-4}	0.20
Sodium dodecyl sulfate	Surfactant	5.5×10^{-3}	1.60
Dodecanethiol	Chain transfer agent	8.3×10^{-4}	0.169

Table 2.5 Materials involved in the polymerization of poly(I-*co*-NaSS) using potassium persulfate and SDS at 60 °C

Table 2.5 shows the components added for the polymerization of poly(I-co-NaSS) using a thermal initiator. The polar components (water, NaSS, sodium dodecyl sulfate) were placed into a 300 ml Parr reactor and the system was sealed and purged with argon for five minutes. The organic components (isoprene and dodecanethiol) were combined and added via syringe into an inlet tube. The mixture was heated to 60 °C and stirred for 12 hours. This method has been outlined in numerous publications[1–5], however the efforts made for the research were not reproducible. Changes were made to the procedure in order to achieve polymerization. These included changing length of polymerization, the temperature of the reaction, the levels of initiator, type of surfactant,

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etc. Also, extra measures were taken to purify the isoprene monomer including multiple

passes through an aluminum oxide column prior to mixing in the separatory funnel. The

result of of the failed polymerizations produced two layers of components that never

polymerized as shown in Figure 2.7. It was determined that the likely cause of the failed

reactions was a leak somewhere within the Parr reactor system that was allowing

oxygen to enter, which inhibited polymerization. This lead to the utilization of the redox

initiators (as outlined in section 2.3.2)

Figure 2.7 Failed poly(I-*co*-NaSS) polymerization material

2.9 Chapter two supplemental information references

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Chapter 3. Conclusions and Future Work

3.1 Thesis conclusions

The objective of the discussed research was to utilize free radical emulsion polymerization to polymerize an isoprene-sodium styrene sulfonate ionomer with varying amounts of the ionic sodium styrene sulfonate. Once polymerization was successfully completed, the objective was to chemically characterize the ionomers and to determine the structure-property relationship of the polymer as the ion concentration was increased. From the successful polymerizations, chemical characterizations and determinations of the different properties, many conclusions could be made.

Based on the evidence, the synthesis the poly(I-*co*-NaSS) polymers was dependent upon an oxygen free environment. Initial attempts at polymerization inside of a Parr reactor were unsuccessful and it is hypothesized that this was due to oxygen entering the system. Once an oxygen-free environment could be maintained, the polymerization was successful and polymers with ion concentrations that were accurate, in relation to the theoretical and measured sulfur percentages, were produced. Unlike previous publications[1], FTIR results could not be used quantitatively, but the S=O stretching peak qualitatively depicted the increase in peak height as the concentration of NaSS increased. While the molecular weight of the ionomer could not be determined, it is confirmed that the molecular weight is high. Unfortunately, the aggregate size, as measured by dynamic light scattering (DLS) in solution could not be determined, as the aggregates were too large and the polydispersity index was too high.

The morphological results, as measured by small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) allowed for several deductions to be made about the poly(I-*co*-NaSS) series of polymers. The SAXS data indicate that there is no distinct ionic aggregate peak. This coupled with the lack of a systematic T_g change with ion concentration increase, indicates that there is an absence of ionic aggregation.

While the morphological properties remained similar throughout the series of polymers, the mechanical properties showed drastic differences as the ion concentration was altered. Both the stress-strain and stress relaxation behavior suggest that as the ion concentration increases the strength of the polymer also increases. The hysteresis results indicate that in the linear region of the stress-strain plot the behavior of the polymers are very similar.

3.2 Future work

3.2.1 Polymerization using vinylbenzylchloride and different cations and anions

To observe changes to the polymer morphology based on the chemical structure of the polymer, a different method of polymerization can be tested. Figure 1 shows the reaction that would take place if isoprene was first polymerized with vinylbenzylchloride (VBC) followed by the addition of the ionic group. The ionic group could be either anonic (sulfonate or carboxylate) or cationic (phosphonium or ammonium) and stabilized with varying counterions.[2–5] This type of reaction would give evidence of how a random copolymer with VBC would polymerize as opposed to an ionic monomer, as was studied in this research.
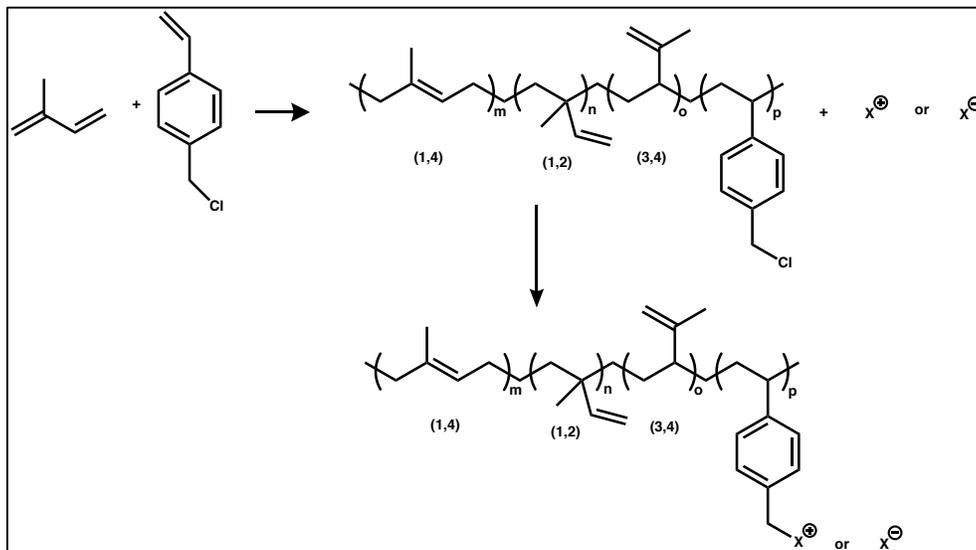
Figure 3.1 Proposed reaction for alternative pathways to creating an ionic polyisoprene copolymer

3.2.2 Mechanical testing with altered relative humidity

The presence of ions within a polymer can lead to changes within the properties of the polymer when it is introduced to humidity. It would be of interest to determine the mechanical properties as the ion concentration changes as well as how the properties change as the humidity is increased. This type of experiment has been performed for polymers containing ions and the property changes can be quite drastic.

3.2.3 Small angle X-ray scattering at different strains

Figure 2 shows the stress-strain behavior found for the series of poly(I-co-NaSS) polymers. A consistent trend for the polymers with the highest ion concentrations have an increase in the slope at approximately 750 percent strain with leveling off again at approximately 1700 percent strain. These changes could be due to changes in the way the ions are interacting with one another as the polymer is stretched. If the system is chemically cross-linked, the ions would have no way to interact with one another, due to the chemical network holding them apart. When stretching the polymer, these ions may

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then have a way to come into contact with one another, and create an increase in

strength in the form of temporary ionic aggregates. A way to observe this morphological

change would be to determine the phase behavior of the polymer by using small angle

X-ray scattering (SAXS) while the polymer is being stretched.
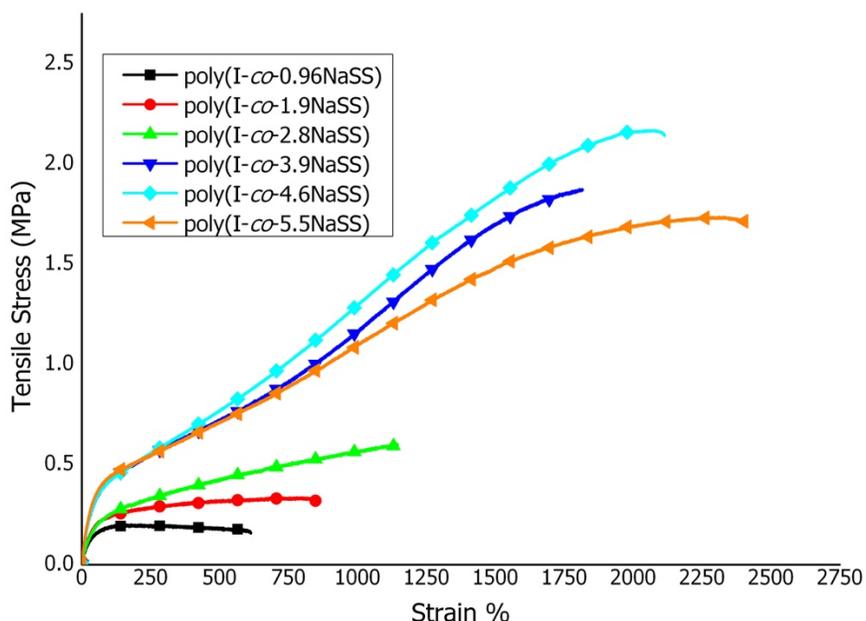
Figure 3.2 Stress vs strain behavior for a series of poly(I-*co*-NaSS) samples

3.2.4 Hysteresis at different strain percents

The hysteresis data obtained for the polymers is shown in Table 3.1. The data

indicate that the series of polymers behave similarly while in the linear region of the

stress-strain curve. However, observing the entire stress-strain curve (Figure 2), it can

be assumed that the hysteresis behavior could vary for each polymer in the series if

taken to higher percent strains prior to beginning the unloading portion of the hysteresis

cycle. Prior research has shown that a series of hysteresis measurements can be taken

at different strain percentages and compared in order to determine the behavior of each

polymer as the strain increases.[6,7]

sample	Maximum strain (%)	% Hysteresis First Cycle	Avg. % Hysteresis Second-Fifth Cycles
poly(I-*co*-1.2NaSS)	25	29.0	27.8 ± 0.4
poly(I-*co*-1.6NaSS)	30	25.5	23.8 ± 0.3
poly(I-*co*-2.6NaSS)	30	23.0	21.2 ± 0.2
poly(I-*co*-3.4NaSS)	40	21.7	19.2 ± 0.1
poly(I-*co*-4.6NaSS)	40	24.6	22.2 ± 0.2
poly(I-*co*-4.7NaSS)	45	26.5	23.4 ± 0.4

Table 3.1 Hysteresis results for poly(I-*co*-NaSS) copolymers

3.3 Chapter Three References

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