RHEOLOGY OF OLIGOMERIC SULFONATED POLYSTYRENE IONOMERS

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ABSTRACT

Ionomers are flexible polymers containing small amount of ionic groups. Those ionic groups endow ionomers with excellent physical and mechanical properties. In order to understand the ionomer dynamics, oligomeric sulfonated polystyrene (SPS) ionomers were selected as a model system due to the absence of chain entanglement.

Firstly, the gel point of SPS ionomers was determined as the degree of sulfonation $p = p_c$, corresponding to one ionic group per chain on average. Below the gel point, ionomer behaves like a sol. Close to the gel point, characteristic power law relaxations occur. Above the gel point, ionomers show a plateau in the $G'$. Based on the mean field theory, a reversible gelation model with only two parameters, the Rouse relaxation time of the Kuhn segment $\tau_0$ and ionic dissociation time $\tau_s$, was developed. This model predicts well the LVE behavior of SPS ionomers. The $\tau_0$ increases linearly with the increasing $p$ but remains unchanged for different metal cations. The $\tau_s$, however, increases with decreasing radius of alkali metal cations due to the increased Coulomb energy. While for alkaline metal cations, $\tau_s$ increases with increasing cation radius possibly due to restricted mobility of large divalent cations. For divalent transition cations, $\tau_s$ is highly related to the electron configuration of $d$ orbital of the cation due to the formation of covalent bonds.
Secondly, it was found that binary ionomer blends show identical $p_c$ and similar power law relaxations with neat ionomers. However, even at the same $p$, the blends exhibit a longer terminal relaxation time but a lower plateau modulus due to their broader relaxation time spectrum. The excellent model predictions for LVE behavior of blends indicate that the mixing of alkali cations follows a simple mixing rule: the ionic dissociation frequency, i.e. the reciprocal of $\tau_s$, for the blend is the number average of the two component cations.

Thirdly, the nonlinear rheology of SPS ionomers were investigated with $p < p_c$, $p \sim p_c$, and $p > p_c$. When $p < p_c$, the ionomer exhibits shear thinning behavior. When $p > p_c$, evident melt fracture occurs. Only when $p \sim p_c$, shear thickening emerges. The magnitude of shear thickening increases with the decrease of temperature, cation radius, and the molecular weight of SPS, due to the increased contrast between $\tau_s$ and $\tau_0$.

Fourthly, it was found that the $\tau_s$ of partially neutralized SPS ionomers is controlled by the neutralization degree, $x$, rather than the $p$. Increasing $x$ enhances $\tau_s$ especially near complete neutralization. The $\tau_s$, predicted from the dielectric behavior, agrees well with those obtained from rheology. This indicates that the plasticization effect of acid groups is to soften the ionic interaction between metal sulfonates.

Lastly, the covalent crosslinking was found to greatly reduce the creep compliance of ZnSEPDM/ZnSt compounds especially at high $T$ and high loadings of ZnSt due to the suppression of ion-hopping process. Therefore, the shape memory performance was greatly improved after covalent crosslinking.
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CHAPTER I

INTRODUCTION

Polymers play an essential and ubiquitous role in our daily life owing to their versatility, functionality and affordability. In order to meet the special needs in specific applications, non-covalent bonding, including ionic interaction, hydrogen bonding and van der Waals, was incorporated into polymer chains to tune the structure and properties of polymeric materials. Ionomer, defined as a flexible polymer containing less than 15mol% of covalent attached ionic groups, has attracted widespread interest in the past several decades. The presence of the ionic interaction endows the ionomers with excellent physical, mechanical and rheological properties. For example, the poly(ethylene-co-methacrylic acid) (PEMA) ionomer, developed by DuPont under the trade name Surlyn at 1960s, has been widely used as packaging films, sports goods and polymer blend compatibilizers owing to its outstanding clarity, toughness and tensile strength.¹

The polar ionic groups of the ionomers usually associate with each other and form nanometer-sized ionic aggregates in the nonpolar medium due to their strong ionic interactions. Those ionic aggregates behave as physical crosslinks, and significantly alter the dynamics of ionomers. An in-depth knowledge of the effect of ionic interaction on the rheological behavior of ionomers is crucial for their processing and manufacturing. It will
help to find the optimum conditions for melt processing of ionomers, such as the processing temperatures, rotation speed of the screw and production rate. Despite their wide application, the understanding of the rheological behavior of ionomer melts is still quite limited. Herein, the main objective of this study is to understand the effect of ionic interaction on the linear and nonlinear rheological behavior of ionomers, and then predict them with simple viscoelastic models.

Although rheological behavior of ionomers has been extensively studied and reviewed by Register and Prudhomme\textsuperscript{2}, most of the ionomers investigated so far were highly entangled, where the ionic interaction is often complicated by the presence of chain entanglement. In order to isolate the effect of the ionic interactions, oligomeric sulfonated polystyrene (SPS) ionomers was adopted as a model system for the study of the rheology of ionomers. In this approach, the long time or high temperature relaxation behavior is mainly affected by the ionic interaction because the molecular weight of SPS ionomers is far below the entanglement molecular weight of polystyrene (PS).

In the first part (Chapter III), oligomeric SPS ionomers with different sulfonated degrees were synthesized from two PS precursors with different molecular weight, where both molecular weights are below the entanglement molecular weight. After neutralized with different alkali metal cations, their linear viscoelastic (LVE) behavior was investigated, and compared with the predictions from a newly developed reversible gelation model.

In the second part (Chapter IV), the applicability of the reversible gelation model was investigated in the binary blends of two SPS ionomers with same molecular weight but
different sulfonation degrees and metal cations. The effects of the average sulfonation degrees and different combinations of metal cations on the LVE behavior were investigated. If a linear mixing rule was utilized to quantify the mixing of metal cations, a reasonable prediction of LVE behavior can be achieved with the reversible gelation model.

In the fourth part (Chapter V), the nonlinear rheological behavior of SPS ionomers with different molecular weight, various sulfonation degrees and metal cations were examined. A shear thickening behavior was found for SPS ionomers with ionic content close to the gel point, defined as one ionic group per chain on average, and neutralized with certain metal cations at certain temperature ranges.

In the fourth part (Chapter VI), the LVE behavior of partially neutralized SPS ionomers was analyzed with reversible gelation model and compared with their dielectric behavior. The unneutralized sulfonic acid groups was found to serve as an ionic plasticizer, promoting the terminal relaxation of ionomers. And that plasticization effect mainly originates from the increase of the polarity, i.e. the increase of dielectric constant, within the ionic aggregates.

In the fifth part (Chapter VII), the LVE behavior of SPS ionomers fully neutralized with alkaline earth and divalent transition metal cations were studied with degrees of sulfonation below, close to, and above the gel point. The effect of divalent cation on the LVE behavior was discussed with respect to cation radius, electron configuration, and the ionic dissociation time obtained from the predications of the reversible gelation model.

In the sixth part (Chapter VIII), the viscoelastic behavior, especially the creep
behavior, of blends of sulfonated poly[ethylene-r-propylene-r-(5-ethylidene-2-norbornene)] (SEPDM) and zinc stearate (ZnSt) with and without covalent crosslinking was investigated under different temperatures and ZnSt loadings. ZnSt decreases the creep compliance of the SEPDM/ZnSt blends at temperatures below the melting point, but significantly increases the creep compliance when ZnSt melts at high temperature due to its plasticization effect. This incorporation of covalent crosslinking could suppress the plasticization effect, decrease the creep compliance, and thus improve shape recovery performance.
CHAPTER II

BACKGROUND

Unlike polyelectrolyte, where almost every monomer contains ionic group, ionomers are actually copolymers of nonionic monomers and a small amount, typically less than 15%, of ionic monomers. Because of the presence of ionic groups, ionomers possess phase separated structure and unique physical and mechanical properties. The structure and properties of ionomers can be tuned and controlled by a series of different parameters, including the type of ionic groups, the concentration of ionic groups, and the distribution of ionic groups along the polymer chains. Owing to its wide application, the structure property relationship of ionomers has been the subject of academic and industrial research for the last 60 years. This chapter summarizes some of major findings in the synthesis, structure characteristics, thermal properties and rheology behavior of ionomers.

2.1 Synthesis of ionomers

Based on the distribution of the ionic groups, ionomers can be classified into three main groups: random ionomers, telechelic ionomers, and precise ionomers. The random ionomers mean that the ionic groups, or ionic monomers, are randomly distributed along the polymer chains. The telechelic ionomers refer to the ionomers whose ionic groups are selectively located at both chain ends. While the precise ionomers contain ionic monomers
separated by precisely controlled number of nonionic monomers.3

There are two major methods to synthesize random ionomers: the direct copolymerization of ionic and nonionic monomers, and the post-polymerization modification of the polymer precursors. For example, Weiss et al.4-6 used an emulsion copolymerization to directly synthesize sulfonated ionomers from the copolymerization of sodium styrene sulfonate monomer and a nonionic monomer, such as styrene4, 5 and butadiene6 monomer. However, the direct copolymerization method has some major problems, for example, the difficulty to dissolve both ionic and nonionic monomers in the same solvent, to control the molecular weight and molecular weight distribution of the result ionomers, and the poor compatibility of the ionic monomers with polymerization techniques.7, 8 In order to solve these problems, the ionic groups in the ionic monomer are sometimes protected through converting the acid groups into esters or salts before the copolymerization. Conventional free radical polymerization and controlled radical polymerization, such as RAFT and ATRP7, 9, have been to synthesize ionomers with well-controlled structure and molecular weight, such as sulfonated PLA ionomers10, 11, carboxylated poly(butyl acrylate) ionomers12, and phosphonated polystyrene ionomers.13

The post-polymerization modification method, modifying the polymer precursors through post reaction including sulfonation14-19 or carboxylation20, 21 reaction, is another widely used method to synthesize random ionomers. For instance, Makowski et al.14 introduced a simple method to synthesize lightly sulfonated polystyrene in a solution of
dichloroethane (DCE) by reacting polystyrene with a sulfonation agent, acetyl sulfate. Acetyl sulfate was freshly prepared from the reaction of concentrated sulfuric acid and acetyl anhydride at \( \sim 0^\circ C \) before adding into the polystyrene solution. Figure 2.1 shows the schematic illustration of this sulfonation reaction. After sulfonation, the result ionomers can be easily neutralized into different salts.

![Reaction scheme of sulfonation](image)

Figure 2.1 Reaction scheme of sulfonation: (a) acetyl sulfate generation, (b) sulfonation of polystyrene and neutralization of sulfonated polystyrene.

This method was also used in the sulfonation of other benzene ring containing polymers, including poly (2,6-dimethyl-1,4-phenylene oxide) (PPO), ethylene-propylene-diene monomer terpolymer (EPDM), and poly(styrene-ethylene/butylene-styrene) (SEBS). However, the sulfonation of some other benzene ring containing polymers, such as poly(ether ether ketone) (PEEK), require a harsher sulfonation agent, such as concentrated sulfuric acid and chlorosulfonic acid.

The other two categories of ionomers, i.e. telechelic ionomers and precise ionomers, often requires a careful control of the polymerization. Living anionic polymerization technique is typically used to the prepare telechelic ionomers, including sulfonated...
polyisobutylene ionomers\textsuperscript{22, 23}, carboxylated polyisoprene\textsuperscript{24} and polybutadiene\textsuperscript{25, 26} ionomers. Sometimes, a post modification is needed to convert protected end groups into active ionic groups, such as acids and salts. Recently, precise ionomers were successfully synthesized by acyclic diene metathesis (ADMET) polymerization methods.\textsuperscript{3, 27} For example, precise polyethylene ionomers with both carboxylate and phosphonate pendent groups evenly distributed along the polymer chain were synthesized by Baughman et al.\textsuperscript{3} and Buitrago et al.\textsuperscript{27}, respectively, and the structure and properties can be controlled through varying the number of carbon groups between neighboring ionic groups. However, only precise polyolefin ionomers were synthesized so far because of the limitation of the ADMET method.

Compared to the other two types of ionomers, random ionomers are much easier to synthesize, and they have attracted a lot of interests from academic and industrial researchers. In this study, the major focus is to investigate the rheological behavior of random ionomers, including sulfonated PS and sulfonated EPDM. Therefore, in the following sections, the studies of random ionomers were summarized with respect to their structure, thermal properties, and rheological behavior.

2.2 Structure and thermal properties of random ionomers

The strong dipolar or ionic interactions between ionic groups produce nanometer-sized ionic aggregates dispersed in the polymer matrix. The presence of ionic aggregates increases the glass transition temperature of the ionomer and is responsible for the unique
physical and mechanical properties of ionomers. This section will cover the molecular structure characteristics, morphology theories, and thermal properties of random ionomers.

2.2.1 Phase structure

The microstructure of the ionomers has been extensively evaluated by a series of different analytical techniques, including small angle X-ray/neutron scattering (SAXS/SANS)\textsuperscript{28-39}, transmission electron microscopy (TEM)\textsuperscript{40-44}, Fourier transform infrared spectroscopy (FTIR)\textsuperscript{45, 46}, extended X-ray absorption fine structure (EXAFS)\textsuperscript{47}, and electron spin resonance (ESR)\textsuperscript{48}. Although a phase separated structure was observed by most of the techniques, the size, distribution, and composition of the ionic aggregates is still not fully understood.

SAXS is the most widely used technique in the research of ionomer morphology, and it has provided the most convincing evidence for the microphase separated structure of ionomers. Typically, the SAXS curves of ionomers exhibit a maximum at a $q$ range of $q = 1 - 3$ nm$^{-1}$ when the ionic concentration is above a critical value, where $q$ is the scattering vector, $q = 4\pi\sin\theta/\lambda$, with $\lambda$ as the wavelength of the radiation and $2\theta$ as the angle between the scattered and incident waves.\textsuperscript{49} This maximum, often referred to as the ionic peak, originates from the large difference in the electron density between the ionic aggregates and hydrocarbon polymer backbone.\textsuperscript{50} At low $q$, the SAXS curves of ionomers exhibit an upturn in the scattering intensity. Register and Cooper\textsuperscript{31, 51} used anomalous small angle X-ray scattering to study the morphology of nickel neutralized sulfonated polystyrene, and
they attributed the scattering upturn to the inhomogeneous distribution of isolated ionic
groups throughout the polymer matrix rather than unneutralized acids or excess
neutralizing agent. It was reported that the addition of excess neutralization agents
decreases the upturn scattering intensity, but increases the intensity of the ionic peak
because the neutralizing agent is absorbed into the ionic aggregates.\textsuperscript{31}

Many morphology theories have been proposed to account for the ionic peak observed
in the SAXS curve.\textsuperscript{52} However, no model does a perfect job at describing the size,
distribution, and shape of the ionic aggregates.\textsuperscript{53} Among those models, the modified hard-
sphere (MHS) model, proposed by Yarusso and Cooper\textsuperscript{28}, provides an excellent prediction
for the ionic peak in SAXS, although it fails to fit the low $q$ upturn. As shown in Figure
2.2, the MHS model assumes that the ionic aggregates are arranged with a liquid-like order,
and each ionic aggregates is coated by a hydrocarbon material shell with a thickness of $R_{CA}$
-$R_I$, where $R_{CA}$ is the closest approach distance between two ionic aggregates and $R_I$ is the
size of the ionic aggregates.
Figure 2.2 Schematic of modified hard sphere model and corresponding electron density profile for one of the particles. Reprinted with permission from ref. 28. Copyright © 1983, American Chemical Society.

Figure 2.3 shows an example of the fit of the SAXS curves of sulfonated polystyrene partially neutralized with zinc (Zn). For all different sulfonation degrees, the MHS model predicts well the ionic peak but it does not predict the intensity in the low $q$ range. With increasing sulfonation level, the ionic peak increase in intensity, but the position of the SAXS maximum is nearly insensitive, which is consistent with the model prediction that a size of the ionic aggregates ($R_I$) of about 2.0 nm in diameter and the $R_{CA}$ of around 3.4 nm are obtained for all the Zn-SPS ionomers. Some other studies of SPS ionomers also reported that changing the cation or neutralization degree does not significantly affect the position of the ionic SAXS peak or the size of aggregates, but does significantly alter the
intensity of the peak owing to the different electron density of different cations and the free acids.\textsuperscript{32, 34, 35}

Figure 2.3 Fitting of modified hard-sphere model (solid lines) to experimental SAXS data for 85% neutralized Zn-SPS: (A) 1.68 mol\%, (B) 3.37 mol\%, (C) 5.55 mol\%, and (D) 6.91 mol\%. Reprinted with permission from ref. 28. Copyright © 1983, American Chemical Society.

Weiss and Fitzgerald\textsuperscript{53, 54} investigated the effect of plasticizers, glycerol and dioctyl phthalate (DOP), on the structure of sulfonated polystyrene ionomers. It was found that the nonpolar plasticizer, DOP, decreased the intensity of the ionic peak but had little effect on the shape and position of the peak. The polar plasticizer, glycerol, increased the ionic peak intensity and shifted the peak to lower $q$ due to the solvation of the ionic aggregates. Similar phenomena were also observed for zinc sulfonated EPDM/zinc stearate (ZnSt) composites,
where the ionic peak was shifted to low $q$ when ZnSt melted and served as a plasticizer.$^{55}$

![Schematic diagram](image)

**Figure 2.4** Schematic diagram of the region of restricted mobility surrounding a multiplet in a poly(styrene-co-sodium methacrylate) ionomer. Reprinted with permission from ref. 56. Copyright © 1990, American Chemical Society.

In order to explain the dynamic mechanical behavior and X-ray scattering of random ionomers, Eisenberg et al.$^{56}$ proposed a multiplet-cluster model (also referred to as the EHM model). This model is based on the concept of multiplets, which is defined as an ionic aggregate formed by several ion pairs. At the surface of each multiplet, there is a restricted mobility layer, where the mobility of the polymer chains is significantly reduced by the ionic interactions (Figure 2.4). The thickness of this restrict mobility layer is
estimated to be the order of the persistence length of the nonionic polymer. In general, the restricted mobility layer is too small to have its own glass transition, but it can increase the $T_g$ of the polymer matrix. As the ionic content is increased the restricted mobility layers for multiple multiplets may overlap with each other. When this overlap becomes frequent, large regions of restricted mobility form. When these regions becomes sufficiently large, they exhibit their own $T_g$, and are termed clusters.

TEM has been used to directly observe the size, shape, and distribution of the ionomer aggregates. Winey et al. used scanning transmission electron microscopy (STEM) to investigate the nanoscale morphology of partially neutralized Zinc-poly(ethtlene-ran-methacrylic acid) ionomers and found that the spherical ionic aggregates are ~2 nm in diameter and independent of the neutralization level. In sulfonated polystyrene ionomers, the ionic aggregates also show a size of ~2 nm in diameter for Zn, Cs, and Ba salts. More recently, the nanoscale morphology of Zn neutralized sulfonated polystyrene was investigated by a three-dimensional reconstruction methods. It was found that the melt an ionomer that was fabricated by compression molding in melt showed heterogeneously distributed spherical aggregates with an average diameter of ~5 nm, while the ionic aggregates in a solvent-cast ionomer formed nano-platelets with a thickness of ~6 nm (Figure 2.5).
2.2.2 Glass transition

Generally speaking, the incorporation of the ionic groups restricts the chain mobility of polymer backbone and increases the glass transition temperature, $T_g$, of the polymer matrix. However, the change of $T_g$ is highly dependent upon the ionic content and the type of counterion.

Weiss et al.\textsuperscript{58} systematically investigated the effect of counterion and ionic content of the $T_g$ of the lightly sulfonated polystyrene ionomers. They found that the $T_g$ was only a function of the ionic content for both free sulfonic acid, Zn salts, and ammonium salts derivatives, as shown in Figure 2.6.\textsuperscript{58} Yang et al.\textsuperscript{59} reported that $T_g$ of SPS ionomers was independent of the metal cation for alkali, alkaline earth and rare earth metals. However, for soft counterions, such as aliphatic amines, the $T_g$ of SPS ionomers is significantly
affected by the length of the alkyl chains and the number of substitutes in the ammonium counterion. In particular, when the amine counterion was sufficiently bulky, the $T_g$ of SPS ionomers actually decreased with the increasing ionic content.\textsuperscript{58}

Figure 2.6 The effect of sulfonation degree on the $T_g$ of sulfonated polystyrene for (○) the free acid, (□) zinc salt, and (△) ammonium salts. Reprinted with permission from ref. 58. Copyright © 1984, John Wiley & Sons, Inc.

When the ionic content is high enough ionic cluster forms. Those clusters exhibit their own glass transition temperature. Eisenberg et al.\textsuperscript{60} investigated the dynamic mechanical properties of the SPS and poly(styrene-co-sodium methacrylate) (PSMA) ionomers and attributed the second loss tangent peak to the glass transition of the cluster phase. As depicted in Figure 2.7, for both SPS and PSMA ionomers, the $T_g$s of the polymer matrix and cluster phase increase linearly with ionic content. The cluster phase exhibits a much
higher $T_g$ than that of polymer matrix and the increase of $T_g$ with ionic content is greater for the former.$^{60,61}$ For the same ionic content, the SPS ionomer shows a cluster $T_g$ of ~60°C higher than PSMA ionomers, indicating stronger ionic interactions between sulfonate groups than those between carboxylate groups. The cluster $T_g$ was not detected for the poly(styrene-co-N-methyl-4-vinylpyridinium iodide) copolymers from dynamic mechanical analysis, which might be attributed to the large size of the cation and anion groups, and the restricted mobility of the ionic groups due to the relatively high $T_g$ of the polymer matrix.$^{62}$

Figure 2.7 Glass transition temperature obtained from loss tangent peak at 1 Hz for a number of random styrene ionomers. Open symbols indicate low $T_g$ phases, and filled symbols indicate cluster phases. Reproduced from ref. 60, Copyright © 1992, American Chemical Society.
2.3 Rheological behavior of random ionomer melts

The melt rheological behavior of random ionomers is highly affected by the presence of ionic aggregates. Those ionic aggregates serve as physical crosslinks, restrict the motion of the ionomer chains and delay the relaxation times. Unlike covalent crosslinks, at high temperatures or long time an ionic group can dissociate from the ionic aggregates and then re-associate back to the original aggregate or move to a neighboring aggregate. This process allows the melt flow of the ionomer, and is often called “ion-hopping”.63, 64 However, the viscosity of the ionomers is usually quite high owing to the long relaxation times of the ionic association. A review on the rheological behavior of random ionomer melts was published by Register and Prud’homme in 1997. In the last twenty years, much research has been devoted to the understanding of the rheological behavior of ionomers. In this section, linear and nonlinear rheological behavior of random ionomer melts are briefly discussed with respect to different ionic concentration, type of cation, neutralization degree, and the effect of plasticizers. Some studies of telechelic ionomers are also included for comparison.

2.3.1 Time temperature superposition

Linear viscoelastic (LVE) behavior of ionomer melts is often investigated using small amplitude oscillatory shear (SAOS). During the SAOS experiment, a sinusoidal strain or stress with small amplitude is applied to the ionomer, and the corresponding stress or strain response is detected, and converted into mechanical properties, such as dynamic modulus
and complex viscosity. With the help of time temperature superposition (TTS), the relaxation behavior of ionomers can be obtained over a large time scale, though TTS does not work very well for many ionomers.

Agarwal et al.\textsuperscript{65} investigated the effect of metal sulfonate groups on the melt rheology of entangled sulfonated EPDM (SEPDM) ionomers. After sulfonation, the temperature range of the rubbery plateau was extended from less than 30\degree C for EPDM to over 100\degree C for Zn sulfonated SPEDM ionomers. Increasing the amount of Zn sulfonate groups further extended the plateau region, and increased the plateau modulus, as well. TTS was found to be applicable for Zn sulfonated SPEDM ionomers, and the shift factors were described well by the WLF equation. The WLF constants of ionomers differed slightly from neat EPDM and SEPDM ionomers with sulfonation levels between 0.7 and 1.5 mol\%\textsuperscript{65}

Weiss et al.\textsuperscript{66} investigated the effect of ionic concentration on the linear viscoelastic behavior of entangled SPS ionomers (Figure 2.8). The increase of sulfonation level increased the plateau modulus and for a fixed temperature shifted the terminal relaxation to lower frequency due to the increased crosslink density of the physical network formed by the ionic interactions. Although $T_g$ increased slightly with increasing sulfonation degree, the dynamic modulus in the glassy region remained almost the same at $T_r = T_g$. In addition, TTS worked quite well for this system over a value of reduced frequency that spanned nearly 20 orders of magnitude. In a later study of entangled SPS ionomer ($M_w = 400$kg/mol), TTS also worked well for different counterions (including Na and NH$_4^+$) and a range of
sulfonation degree from 0.11 to 1.71 mol%<sup>67</sup>. The reason for the success of TTS was attributed to the large difference between ionic relaxation time and segment relaxation time, thus both relaxation processes were not observed in a single experiment.<sup>32</sup>

For carboxylated ionomers, it was found that TTS worked for partially neutralized entangled PEMA ionomers with different metal cations (including Na, Mg, Zn, Ca, and mixtures of them) and different neutralization degrees (typically less than 70%).<sup>63, 64, 68-70</sup> Furthermore, a super master curve was obtained through shifting master curves of PEMA with different metal cations horizontally.<sup>69, 70</sup> Those obtained super shift factors depended on the type and the composition of the metal cations.<sup>68-70</sup> One reason for the success of TTS in the PEMA or PEAA system is that the two relaxation processes: ionic dissociation and the segmental relaxation, may be well separated in time,<sup>63, 64</sup> which is similar to the case of entangled SPS ionomer.<sup>66, 67</sup> Another reason is that the presence of acid groups promotes the ionic dissociation so that the difference in the temperature dependences of both relaxation processes may become too small to be observed in this entangled ionomers.

In general, the failure of TTS is commonly observed for most ionomers due to the different temperature dependences of the ionic relaxation time and segmental relaxation time.<sup>71</sup> However, in some ionomers, TTS only fails when the ionic content is above certain values. Below the critical ionic content, the effect of ionic relaxation is relatively weak, and the relaxation is mainly controlled by the segmental relaxation. When above the critical ionic content, the ionic relaxation starts to dominate the relaxation behavior at higher
temperatures or low frequencies, leading to the failure of TTS. For example, TTS failed in entangled poly(styrene-co-sodium methacrylate) (PSMA) ionomers only when the ionic content is above 7.7 mol% \(^{72, 73}\), in entangled poly(ethylene-co-acrylate) (PEAA) ionomers when >12 mol% of ionic groups was incorporated\(^{74}\), and in entangled sulfonated poly(ethylene terephthalate) (SPET) ionomers containing >10 mol% of the sulfonate groups.\(^{75}\) In addition, the polyester ionomers, copolymers of polyethers (PEO and PTMO) and sodium sulfonated phthalates, only exhibited a very weak failure of TTS in the glassy–rubbery transition region.\(^{76, 77}\) However, a clear transition in the temperature dependence of the shift factor was clearly observed. The high temperature shift factors exhibited an Arrhenius–like temperature dependence, which is associated with the ionic relaxation, while the low temperature shift factor is related to the segmental relaxation, thus showed a WLF-like temperature dependence.\(^{76, 77}\) In some other studies of SPS, PSMA and PEMA ionomers\(^{32, 78-80}\), TTS worked for \(G'\) but failed for \(G''\) because \(G''\) is more sensitive to the different relaxation behavior. Similar phenomenon was also observed in the sulfonated styrene-ethylene-butene (SSEB) ionomers\(^ {21, 81}\) and poly(styrene-co-vinylphosphonate) (SVP) ionomers,\(^ {82}\) where TTS failed for both \(G'\) and \(G''\) with a severer failure occurred in \(G''\).
2.3.2 Effect of ion type and ion content

As discussed above, the dynamics of ionomers is mainly influenced by the strength of the ionic association, i.e. the ionic interaction between the bound ion and the counterion. The most common bound ions are acidic groups, such as carboxylate group, sulfonate group, and phosphonate group. While the counterion can be selected from a variety of metal cations, and organic amines etc. In general, it is often quite difficult to change the type of the bound ion, for example, from sulfonate to carboxylate, due to the difficulty of the synthesis. However, for a given acid group, a series of ionomers with tailored properties can be easily obtained through neutralizing acid groups with different counterions.

The effect of bound ion, sulfonate or carboxylate, on the melt viscosity of ionomers was investigated by Lundberg and Makowski. Both carboxylated and sulfonated polystyrenes (CPS and SPS) were synthesized by post-polymerization method with all the
substitution occurring at the \textit{para} site of styrene ring. Figure 2.9 shows the viscosity of these polystyrene ionomers obtained from capillary rheometer for different ionic contents. At similar ionic content, the NaSPS ionomer had a melt viscosity over 2 orders of magnitude higher than that of NaCPS ionomer, indicating a much stronger interaction between sulfonate groups. Visser and Cooper\textsuperscript{83} observed that the sulfonated polyurethane ionomers exhibited higher tensile stress and dynamic modulus than that of carboxylated ionomers when both ionomers were prepared under the identical conditions. Similar result was also observed by Venkateshwaran et al.\textsuperscript{84}, in their study, the stress-relaxation behavior showed that carboxylated telechelic polyisoprene ionomers relax orders of magnitude faster than that of sulfonated ionomers, suggesting a stronger ionic association between sulfonate groups. The difference in the strength of ionic interaction might be due to the fact that sulfonic acid has a lower pK\textsubscript{a} (~1.0) than that of carboxylic acids (pK\textsubscript{a} ~4 - 5), which results in a stronger electrostatic attraction between sulfonate groups.
Figure 2.9 Effect of sodium salt content of melt viscosity of lightly sulfonated PS compared with lightly carboxylated PS at 220°C. Reproduced from ref. 20, Copyright © 1980, American Chemical Society.

However, Register et al.\textsuperscript{21, 81} found that the Li neutralized carboxylated poly(styrene-co-ethylene-co-butene) (SEB) ionomer had a complex viscosity quite similar to that of Na neutralized sulfonated SEB ionomer. Even considering the difference between Na and Li, the type of bound ion group, carboxylate or sulfonate, has very weak effect on the viscosity. The reason for the comparable viscosity of these two ionomers is unknown, which might be attributed to the presence of phase separated structure in SEB copolymers and/or the presence of small crystallites of polyolefin segments.

In addition, Wu and Weiss\textsuperscript{13, 82} synthesized a series of poly(styrene-co-vinyl-phosphonate) (SVP) ionomers with different concentrations of phosphate groups and
compared their LVE behavior with that of sulfonated PS. Although the phosphoric acid (pK$_a$ ~2-3) possesses a relative weaker acid strength than that of sulfonic acid (pK$_a$~1.0), i.e. a higher pK$_a$, both NaSVP and ZnSVP ionomers exhibited a much higher plateau modulus and a much more extended plateau than those of NaSPS and ZnSPS ionomers containing the same amount of ionic groups. This trend was attributed to the steric hindrance effect of phosphonate groups, which were directly attached to the main backbone of SVP ionomers, compared with the sulfonate groups which were attached to the benzene ring of SPS ionomers.$^{13}$

Since the synthesis of ionomers with different bound ions is complicate and time consuming, many researchers tend to change the type of cation in order to tune the viscosity of the ionomers. Weiss et al.$^{58}$ tried to decrease the melt viscosity of SPS ionomers through using neutralization agents with weaker ionic interactions, such as ammonia and alkylamonines. Figure 2.10 shows the melt viscosity obtained from capillary rheometer at 200$^\circ$C for different cations. The melt viscosity could be controlled by changing the number of alkyl chains and the length of the alkyl chain in the ammonium cation. In particular, the tri(n-butyl)ammonium neutralized SPS showed similar melt viscosity with that of PS precursors, but orders of magnitude lower than that of Zn neutralized SPS.$^{58}$
Figure 2.10 Steady shear viscosity versus shear rate at 200°C for SPS261k-2.0 ionomer neutralized with various cations: (▲) Zn, (△) ammonium, (■) n-butylammonium, (●) di(n-butyl)ammonium, (□) free acid, (○) tri(n-butyl) ammonium, and (▽) PS261K. Reproduced from ref. 58, Copyright © 1984, John Wiley & Sons, Inc.

In order to isolate the effect of ionic interaction from the chain entanglement, oligomeric SPS ionomer was adopted to understand the effect of alkali cation on its LVE behavior (Figure 2.9). After neutralization, the terminal relaxation of SPS ionomers was shifted to several orders of magnitude lower frequency. Even for the weakest alkali cation, Cs, the terminal relaxation was delayed by more than 4 orders of magnitude due to the stronger ionic interaction between metal sulfonate groups than acid groups. The plateau modulus $G_N$ of SPS ionomers was independent of the cation type, while the terminal relaxation time SPS ionomers followed the order of $\tau_{Na} > \tau_{Li} > \tau_{K} > \tau_{Rb} > \tau_{Cs}$. Except for the Li salts, the relaxation time for other alkali cations increased with the increase of Coulomb energy of the ion pair, $cq/a$, where $c$ is the ionic content, $q$ and $a$ are the charge.
and radius of the cation, respectively. Similar order of ionic interaction strength for alkali cations has also been observed in other studies of SPS ionomers, and other random ionomers, including SEPDM and PEMA ionomers. The abnormal behavior of the LiSPS ionomer may be attributed to the fact that Li is the smallest cation, and thus Li sulfonate group may be easier to dissociate from the ionic aggregates.

Horrion et al. investigated the master curves of $G'$ and $G''$ for carboxylated telechelic polybutadiene (CPBD, $M_n = 4600$) ionomers, and they found that their terminal relaxation time followed the similar sequence of $\tau_{Na} > \tau_{Li} > \tau_{K} > \tau_{Rb} > \tau_{Cs}$. Stadler et al. studied the LVE behavior of the same CPBD ionomers, but found a completely different trend. The LVE behavior of CPBD ionomers exhibited a strong time dependence. The terminal relaxation time increased by ~3 orders of magnitude after annealing the ionomer to equilibrium. In particular, the equilibrium terminal relaxation time for different metal cations followed a reverse order with $\tau_{Li} < \tau_{Na} < \tau_{K} < \tau_{Rb}$. The reason for this contradictory result in CPBD ionomers is still unknown, and it might be related to the different molecular structure of CPBD ionomer and/or the different sample preparation conditions.
The effect of divalent cations on the LVE behavior of random ionomers becomes rather complex as every cation is connected with two acid groups. In addition, the alkaline earth cations may exhibit different effect on the LVE behavior from those of transition metal cations due to the presence of unfilled $d$ orbital in the latter. Therefore, the ionic strength of divalent cation would probably violate the order of Coulomb energy $c q/a$.

For carboxylated ionomers, Bonotto et al. found that the Ca salts of PEAA ionomers exhibited consistently lower melt indices, i.e. higher melt viscosity, as opposed to Na salts for over a range of neutralization degrees. Sakamoto et al. demonstrated a two times higher viscosity for Ca salt of partially neutralized (56-69%) PEMA ionomers than that of Na salt. Register et al. observed that the Mg and Ca salts of partially PEMA ionomers had a higher melt viscosity than Na salt under different neutralization degrees, which is consistent with other studies of PEMA ionomers. In addition, Nishio et al. investigated the effect of the binary mixture of Na, Mg and Zn cations on the LVE behavior.
of partially neutralized PEMA ionomers. They discovered that the zero-shear viscosity differed for different compositions and combinations of metal cations.\textsuperscript{70}

Jerome et al.\textsuperscript{90, 94} investigated the effect of divalent cation on the dynamic moduli of telechelic CPBD ionomers. They found that the terminal relaxation time for those cations can be ranked as $\tau_{\text{Ba}} > \tau_{\text{Mg}} > \tau_{\text{Ca}} > \tau_{\text{Na}} > \tau_{\text{Zn}}$, with Zn salt exhibited the shortest relaxation time. For carboxylated PDMS ionomers (CPDMS), Batra et al.\textsuperscript{95, 96} observed a strong time-dependent LVE response for Zn, Co, Ba, Ga and Na salts of CPDMS ionomers. The freshly prepared Zn and Co salts exhibited as a viscous fluid, while Ba and Ga salts showed weak network structure. Although the equilibrium modulus was almost the same for both Na and Zn salts, the Zn salt required longer time to reach the equilibrium state due to its weaker ionic interaction.\textsuperscript{95}

In the case of sulfonated ionomers, Agarwal et al.\textsuperscript{65} found that Zn and Pb salts of SEPDM ionomers showed weaker ionic interaction than Cs and Li. However, the two alkaline earth metals, Mg and Ba, showed stronger interaction than alkali metal cations. In addition, the Ba salt exhibited a much stronger ionic interaction than that of Mg salt despite that the former has a larger ionic radius, which violates the relation observed in alkali metals that the terminal relaxation $\tau_d \sim cq/a$. For sulfonated telechelic polyisobutylene ionomers,\textsuperscript{97} it was observed that the melt viscosity of ionomers follows the order of $\text{Zn} < \text{K} < \text{Ca}$, with Zinc salts had the lowest melt viscosity. For SPS ionomers, Hara et al.\textsuperscript{86} showed that the Ca salt had a more extend rubbery plateau than K and Cs salts, indicating
a stronger ionic interaction for divalent cation Ca. Weiss et al.66 calculated the relaxation
time spectra of for Na and Zn neutralized SPS ionomers, and they found that the terminal
relaxation time is around half a decade lower for ZnSPS than NaSPS. Recently, Agrawal
et al.98 used molecular dynamics simulation to study the morphology and melt viscosity of
Na and Mg salts of SPS ionomers. They found the higher viscosity for the Mg salt is related
to the larger aggregate size of the Mg salt.

In general, for divalent cations, Zn would produce the lowest melt viscosity among
all metal cations, while alkaline earth cations often have a melt viscosity higher than that
of alkali cations. One exception is that the Zn salts of partially neutralized PEMA ionomers
have higher melt viscosity than Na salts,63, 64, 68, 99, 100 which will be discussed thoroughly
in Section 2.3.3.

Bagrodia and Wilkes101 attributed the difference between alkaline earth and transition
metal cations to the difference in the electron configuration. In contrary to the ionic bonds
formed between alkali earth cation and acid groups, transition cations tends to form a
covalent bond due to the presence of d orbital in the shell. The filled d orbital (3d10) poorly
shields the nucleus, hence zinc is more polarizable and Zn salts become more covalent.101

Based on the “hard-soft acid” concept, Zn and Pb are soft cations. Therefore, they have a
reduced tendency to associate with the hard ion (SO3−), which results in the weakest ionic
interaction and smallest viscosity.
In addition, the effect of group 4 metal cations (Ti, Zr, Ce) on the LVE behavior of CPBD and Poly(methyl methacrylate-co-methacrylic acid) ionomers was investigated by Broze et al.\textsuperscript{102} and Gotoh et al.\textsuperscript{103}, respectively. It was found that the plateau modulus increased with the size of cations ($r_{\text{Ti}} < r_{\text{Zr}} < r_{\text{Ce}}$),\textsuperscript{102, 103} while the terminal relaxation decreased with the cation radius, exhibiting $\tau_{\text{Ti}} > \tau_{\text{Zr}} > \tau_{\text{Ce}}$.\textsuperscript{102}

2.3.3 Effect of neutralization degree

As discussed above, the cation used to neutralize the ionomer has a significant effect on the rheological behavior because the metal cation often possesses a stronger ionic interaction than the hydrogen (acid form). Therefore, when acid groups are neutralized into metal salts, the ionomer exhibits a longer relaxation time. This offers another method to tune the rheological behavior of random ionomers through neutralizing the acid groups to different degrees. One of the examples is the commercial product Surlyn, where PEMA ionomers were partially neutralized by Na, K, Mg, and Zn with a neutralization degree of $< 90\%$. The existence of the unneutralized acid ionomers ensures an excellent melt processability, while the metal salts groups provides the ionomer with excellent toughness and tensile strength.

Bonotto et al.\textsuperscript{92} found that the mechanical properties of poly(ethylene-co-acrylic acid) ionomers (PEAA) mainly depends on the degree of neutralization rather than the type of metal cations. Increasing neutralization degree results in an increase of modulus and a
decrease of the melt index for both monovalent and divalent metal salts of PEAA ionomers. Spencer et al.\textsuperscript{89} found that the increase of the acid neutralization increased both dynamic modulus and complex viscosity for Na and K salts of PEMA ionomers. Similar results were also observed in Na and Zn salts of partially neutralized SPS ionomers.\textsuperscript{104}

Due to the presence of unneutralized acid groups, the effect of metal cations on the rheological behavior of partially neutralized ionomers becomes even more complex. Those free acid groups could form hydrogen bonding, and hence increase the ionomers’ viscosity by serving as physical crosslinks. For example, the unneutralized SPS ionomers had a viscosity several times higher than that of PS precursor, as studied by Weiss et al.\textsuperscript{32, 58} and also seen in Figure 2.10. Blyler and Haas\textsuperscript{105} discovered that the melt viscosity decreased by four times when 85\% of the acid groups in the PEAA ionomers (containing 5.3 mol\% acrylic acid) were converted to the methyl esters. Similarly, Wu and Weiss\textsuperscript{13, 82} found that after converting phosphonate esters into phosphoric acids, the terminal relaxation of the SVP ionomers was delayed to \(~ 3\) orders of magnitude lower frequency and a weak plateau in the storage modulus occurred before the terminal relaxation due to the presence of hydrogen bonding between acid groups. However, this effect of hydrogen bonding is quite weak compared with the several orders of magnitude of increase in the viscosity when those ionomers are neutralized by metal cations.

The SAXS studies of partially neutralized ionomers showed that the free acid groups tend to associate with the metal salts groups within the ionic aggregates. Register and
Cooper\textsuperscript{31} investigated the SAXS response of nickle (Ni) neutralized SPS ionomers with different neutralization degrees, and they found that the ionomer peak remained unchanged with the change of neutralization levels. Walters et al.\textsuperscript{106} used FTIR to detect the local environment of the unneutralized acid groups in the partially neutralized PEMA ionomers. It was found that those acid groups may interact with each other to form acid dimers, or associate with the salts groups to form a complex. The amount of associated acids increased with increasing neutralization levels, reached a maximum at ~40\%, and then decreased to 0 at ~80\%. The fraction of associated acids also depended on the type of metal cation. For a given neutralization degree, the Zn-PEMA ionomer contained less associated acids than the Li, Na and Ca neutralized PEMA ionomers. The SAXS for the ZnSPS ionomer, at different neutralization levels, revealed that the size of the ionic aggregates are independent of the neutralization degree, and more zinc sulfonate groups are incorporated into the ionic aggregates upon increasing neutralization.\textsuperscript{34}

If free acids are associated with metal salts, the partially neutralized ionomers may exhibit similar LVE response with the blends of highly neutralized ionomer and unneutralized ionomers containing the same amount of metal cations. Otherwise, the ionomer blends may exhibit very different LVE behavior because the highly neutralized ionomer has a viscosity several orders of magnitude higher than that of unneutralized ionomers. Bonotto et al.\textsuperscript{92} compared the mechanical properties of partially neutralized PEAA ionomers with that of PEAA blends, and they found that the partially neutralized
ionomers showed identical melt indices, infrared spectra and mechanical properties with those PEAA.\textsuperscript{92} This indicates that acid groups and metal salts are associated with each other and rapid cation exchange of the metal cation and hydrogen ion occurs during the sample preparation.

Figure 2.12 Zero-shear viscosity at 135 °C for both partially neutralized ionomers (●) and partially esterified ionomers (■). For the partially esterified ionomers, the unneutralized acid groups was converted into ethyl methacrylate. Reproduced from ref. 100, Copyright © 2002, American Chemical Society.

In order to understand the effect of unneutralized acid groups, the melt viscosity of PEMA ionomers was systematically investigated by Register et al.\textsuperscript{63, 64, 100} with respect to different neutralization levels. A portion of the acid groups was firstly neutralized into Na salts. Then the remaining unneutralized acid groups in the partially neutralized samples were converted to ethyl esters. The direct comparison of the melt viscosity of partially neutralized PEMA and esterified PEMA ionomers is depicted in Figure 2.12. At 0%
neutralization, the esterified PEMA had a viscosity five times lower than the PEMA acid due to the elimination of the hydrogen bonding after esterification. However, for partially neutralized samples, the esterified ionomers showed a much higher viscosity than partially neutralized PEMA ionomers especially at lower neutralization degrees. Considering the existence of hydrogen bonding between acid groups, the lower viscosity strongly suggests that those unneutralized acid groups could strongly accelerate the ionic relaxation, exhibiting a strong plasticization effect on the ionic interactions between metal salts.

This result is consistent with the study of Navratil and Eisenberg, who compared relaxation modulus of partially neutralized PSMA ionomers containing equal amounts of Na salts but different contents of free acrylate acid groups, and discovered that extra acid groups did accelerate the stress relaxation, though the effect was not significant. In addition, Navratil and Eisenberg also compared the stress relaxation behavior of a blend of fully neutralized PSMA ionomers with PS and its partially neutralized PSMA ionomers, where both samples contained the same amount of Na salts. It was found that the blend exhibited a rather slower relaxation than the partially neutralized counterpart. If PS is miscible with fully neutralized PSMA ionomers, which was not discussed in the study, this comparison would provide a strong evidence for the plasticization effect of acid groups.

Although the viscosity and relaxation time are mainly controlled by the neutralization degree, the difference between different metal cations is still distinguishable. At high
neutralization levels, the change of metal cation exhibits similar effect with that of fully neutralized samples. However, at low neutralization degree, such as 11-13%, Iwakura and Fujimura\textsuperscript{99} found that Zn salts of PSMA ionomers showed a viscosity of several folds higher than the comparable Na salts. Similar results were widely observed in partially neutralized PEMA ionomers.\textsuperscript{63, 64, 69, 70} For instance, Nishioka et al.\textsuperscript{69} exhibited that the viscosity of ZnPEMA ionomer was \~3 times higher than the Na salts at an identical neutralization degree of 20%. Since Zn\textsuperscript{2+} generally produces the lowest melt viscosity among metal cations, the reason for the higher viscosity is unknown, but one possible reason is that the free acid groups may exhibit weaker plasticization effect on the Zn salts than other metal salts. As discussed earlier, the amount of associated acids is lower for ZnPEMA ionomer than other metal salts of PEMA.\textsuperscript{106} Less associated acids may lead to weaker plasticization effect, and hence a higher melt viscosity.

In addition, Lundberg et al.\textsuperscript{107} showed that the increase of melt viscosity of entangled SPS with increasing neutralization degree experienced an evident transition near full neutralization. As shown in Figure 2.13, melt viscosity increased monotonically when the neutralization degree increased from 0\% to 90\%. Afterwards, a sharp increase in the melt viscosity occurred in the region of 95-100\% with the viscosity increased by over 10 times. The reason for this transition remains unknown, which might be related to the disappearance of the plasticization effect due to the decrease of free acid groups close to 100\% neutralization.
Sometimes, excess neutralizing agents may be used to neutralize an ionomer beyond the stoichiometric point. After the neutralization, the remaining neutralizing agent may associate with the ionic aggregates and affect the LVE behavior of the ionomers. Register and Cooper\textsuperscript{31} studied the SAXS curves of NiSPS with different amount of nickel acetate as neutralizing agent. It was found that the ionomer peak continued to increase beyond 100\% neutralization, suggesting that the excess nickel acetate is absorbed into the ionic aggregates.\textsuperscript{31} Bagrodia et al.\textsuperscript{97,108} reported that the use of 100\% excess of neutralizing agents, such as KOH or Ca(OH)$_2$, increased the melt viscosity of sulfonated polyisobutylene telechelic ionomers (SPIB) by 1-3 orders of magnitude, depending on the
molecular weight and the structure (linear or star) of the telechelic ionomers. However, the addition of excess calcium acetate exhibited little effect on the melt viscosity, and no comparison was made for the Zn neutralized PIB ionomers.\textsuperscript{97, 108} In addition, no similar results has been reported for other random or telechelic ionomers. In fact, Makowski et al.\textsuperscript{17} showed that the increasing amount of zinc acetate (ZnAc\textsubscript{2}) from twice stoichiometric to six times stoichiometric amount decreased the melt viscosity of ZnSEPDM by two times, indicating the plasticization effect of the ZnAc\textsubscript{2} residues and/or the formation of less strongly associating mono-sulfonates, SO\textsubscript{3}Zn\textsuperscript{2+}Ac\textsuperscript{-} at higher ZnAc\textsubscript{2} concentration.\textsuperscript{17} Similarly, in the studies of sulfonated poly(styrene-ethylene/butylene-styrene)\textsuperscript{109} and PSMA\textsuperscript{110} ionomers, the excess of neutralizing agents, such as NaOH and ZnAc\textsubscript{2}, were found to slightly decrease the modulus and promote the ionic relaxation.

To sum up, the increase of neutralization degree significantly enhances the melt viscosity and relaxation time of the partially neutralized ionomers. The presence of free acid groups could serve as a plasticizer and promote the ionic relaxation. Despite those studies, few research has been conducted to understand the LVE behavior of partially neutralized ionomers. Furthermore, the mechanism for the plasticization effect of free acid groups is still unknown.

2.3.4 Effect of plasticizer

Random ionomer melts usually possess very high viscosity because of the long ionic relaxation time. Plasticizer is often added to decrease the viscosity and promote the melt
flow. Since the ionomers have polymer matrix and ion aggregates regions, the ionomers can be selectively plasticized by two types of plasticizers, backbone plasticizer and ionic plasticizer, respectively. A material with low polarity, such as dioctyl phthalate (DOP)\textsuperscript{111} and dibutyl phthalate (DBP), can serve as a backbone plasticizer for the hydrocarbon phase. Those backbone plasticizers promote the segmental relaxation of polymer backbone and lower the glass transition temperature. Ionic plasticizer is typically a material with high polarity, such as glycerol\textsuperscript{111, 112} and water\textsuperscript{113}, and they can selectively weaken the ionic interactions within the ionic aggregates with little or no effect on the nonpolar polymer phase.\textsuperscript{107, 111, 112}

Fatty acid and its salts were found to be excellent ionic plasticizers for the SEPDM ionomers. After melting at elevated temperatures, they could weaken the ionic interaction and promote the melt flow, while at use temperatures, they crystallize and serve as a reinforcer. However, it was found that the efficiency of the plasticization highly depended on the type of the fatty acid salts and the metal cation of the SEPDM ionomers.\textsuperscript{87, 107} Stearic acid faced the problem of compatibility at high loadings (above 10g stearic acid/100g SEPDM).\textsuperscript{87, 107} Barium and magnesium stearate showed little decrease in the melt viscosity (increase in the melt index). While zinc stearate (ZnSt) exhibited the most significant plasticization effect on the melt viscosity of SEPDM ionomers, especially for zinc neutralized SEPDM.\textsuperscript{87} Furthermore, ZnSt also produced a remarkable increase in the tensile strength for Mg, Ba and Zn neutralized SEPDM. In particular, ZnSEPDM/ZnSt
compounds gave the best combination of excellent tensile strength, low melt viscosity and good compatibility up to 60g ZnSt/100g ZnSEPDM. Later, a SAXS study of this system revealed that the ionic peak shifted to lower $q$ after ZnSt melts at high temperatures, indicating the plasticization effect of ZnSt is to swell and dissolve the ionic aggregates.\textsuperscript{55}

Weiss et al.\textsuperscript{111} systematically investigated the effect of backbone and ionic plasticizer on the LVE behavior of NaSPS ionomers. The backbone plasticizer, DOP, lowered the $T_g$ of the polymer matrix and broadened the glass transition temperature. However, DOP did not alter the long time relaxation spectrum associated with the ionic aggregates, which is consistent with the structure feature that the SAXS ionic peak occurs at the same $q$ for different loadings of DOP.\textsuperscript{111} On the other hand, the ionic plasticizer, glycerol, showed little effect on the $T_g$ of the NaSPS ionomers, but shifted the SAXS ionic peak to low $q$. In particular, the long-time ionic relaxation was significantly affected upon the addition of glycerol. Both modulus plateau and the high temperature loss peak disappeared, while the viscoelastic behavior associated with polymer backbone remained unchanged.

In the case of PSMA ionomers, Bazuin et al.\textsuperscript{114, 115} discovered that the addition of non-polar backbone plasticizer, such as polystyrene oligomer ($M_w$ 800) and diethylbenzene shifted loss tangent peaks for both polymer matrix and ionic aggregates to lower temperatures, and increased the contrast between both peak temperatures. Moreover, the addition of polar glycerol slightly decreased the matrix $T_g$ of PSMA ionomers, but contributed to the complete disappearance of the modulus plateau, suggesting the breakup
of the ionic aggregates.\textsuperscript{115} For PEAA ionomers, $T_g$ of polymer matrix and ionic aggregates decreased for both Na and Co salts with the increasing content of non-polar plasticizer 4-decylaniline (4-DA).\textsuperscript{116} When polar glycerol was added, the Co salt exhibited a reduced ionic modulus and a decreased $T_g$ for ionic aggregates due to the disruption of ionic aggregates.\textsuperscript{116}

Kim et al.\textsuperscript{117, 118} studied the effect of sodium salts of organic monoacids and diacids, including sodium hexanoate, sodium adipate, sodium dodecanedioate etc., on the VE behavior of PSMA and SPS ionomers. If the organic salts contain only one acid group, the addition of salts increased the plateau modulus significantly and decreased the $T_g$ of ionic aggregates, serving both as a filler and a ionic plasticizer. However, when its amount exceeds certain concentration, those organic salts became phase separated and acted only as a filler. In contrast, the sodium salts of diacids exhibited no effect on the $T_g$ of polymer matrix or ionic aggregates, and increased the plateau modulus only as an filler.\textsuperscript{118}

Recently, a third type of plasticizer, EO-based plasticizer, was synthesized from end capping nonpolar polymer chains (PEO) with polar groups. This plasticizer showed both backbone and ionic plasticization effect on the ionomers, decreasing the matrix Tg and weakening the ionic interaction within the ionic aggregates at the same time. As depicted in Figure 2.14, both segmental relaxation and terminal relaxation were shifted to higher frequency after the addition of plasticizer.\textsuperscript{119} Compared to pure ionomer, the addition of first 27wt\% of plasticizer shifted the terminal relaxation to 4 orders of magnitude higher.
frequency, while adding another 27wt% only increased the frequency by 2 orders of magnitude. This transition in the plasticization effect was correlated to the transition from an ionomer to a polyelectrolyte due to the solvation of the ionic aggregates. In addition, the acceleration of the ionic dissociation upon the increasing content of plasticizer was quantitatively predicted with the incorporation of the dielectric constant after the segmental $\alpha$ relaxation.\textsuperscript{119}

![Figure 2.14](image)

Figure 2.14 $G'$ and $G''$ master curves as functions of frequency for PEO ionomer and the mixtures with polar plasticizer at reference $T_r = -10^\circ$C with weight percent of ionomer as indicated. Reproduced from ref. 119, Copyright © 2015, American Chemical Society.

### 2.3.5 Rheological theory

A lot of theories has been proposed to understand the rheological behavior of ionomers quantitatively. Among them, Leibler-Rubinstein-Colby (LRC) theory\textsuperscript{120} provides a quantitative treatment for the dynamics of both unentangled and entangled ionomers.\textsuperscript{2}

At times shorter than the lifetime of the ionic aggregates, the entangled ionomers
would behave as elastic rubber with those ionic aggregates serve as physical crosslinks. At longer times, however, the ionomer chain is allowed to diffuse along the confining tube through the breakup of a few physical crosslinks. In the LRC theory\textsuperscript{120}, the effect of ionic network on the stress relaxation behavior was quantified by two parameters: the average fraction of ionic groups associated with the network, the average lifetime of the ionic groups in the associated state, \( \tau_s \).\textsuperscript{120} Figure 2.15 shows schematically the relaxation modulus of entangled nonionic polymers (dashed curve) and ionomers (solid curve) obtained from the scaling analysis. For nonionic polymers, the relaxation modulus is controlled by two major relaxation times, the Rouse time of an entanglement strand \( \tau_e \), and the terminal relaxation time (reptation time) of the total chain

\[
\tau_d = \tau_e \left( \frac{N}{N_e} \right)^3,
\]

where \( N \) and \( N_e \) are degrees of polymerization for polymer chain and entanglement strands, respectively. Between these two relaxation times, nonionic polymer shows the entanglement plateau \( G_2 \). After the incorporation of ionic groups, whose amount is less than 1 per entanglement strand, the ionomer exhibits the same \( \tau_e \), an increased \( \tau_d \), and a transition in the modulus plateau occurring at the ionic network lifetime \( \tau_s \). Before \( \tau_s \), the plateau modulus \( G_1 \) contains the contribution of both entanglement network and ionic network. After \( \tau_s \), the ionic network relaxes, and the plateau modulus drops to \( G_2 \). Following the above analysis, the LRC theory gave an excellent prediction for the terminal relaxation time of ionomers.\textsuperscript{120} However, the predicted transition in plateau modulus (occurring at \( \tau_s \)) was not observed experimentally.
In addition, if the amount of ionic groups is beyond one ionic group per entanglement strand on average, both Rouse relaxation time $\tau_e$ and terminal relaxation time $t_d$ will be greatly delayed by the ionic interaction.\textsuperscript{121} In this case, a good agreement between the relaxation time determined from experiments and predictions from LRC theory was also achieved based on similar scaling analysis.\textsuperscript{121} However, the LRC theory only predicts the scaling behavior of the relaxation time and relaxation modulus of entangled ionomers. A quantitative model for the prediction of the dynamic modulus is still missing probably due to the complexity of the entangled systems.

![Schematic relaxation modulus for nonionic polymers with terminal relaxation time $t_d^0$ (dashed curve) and ionomers with terminal relaxation time $t_d$ (solid curve).](image)

**Figure 2.15** Schematic relaxation modulus for nonionic polymers with terminal relaxation time $t_d^0$ (dashed curve) and ionomers with terminal relaxation time $t_d$ (solid curve). Reproduced from ref.120, Copyright © 1991, American Chemical Society.

The dynamics of unentangled ionomers is much simpler due to the absence of chain entanglement. Based on the scaling approach introduced by LRC theory, Colby et al.
analyzed the scaling relation for the relaxation time of oligomeric ionomers.\textsuperscript{121} Unentangled nonionic polymer chain relaxes through the Rouse motion with the longest Rouse relaxation time $\tau_R^0 = \tau_0 N^2$. For an unentangled ionomers, the longest Rouse relaxation time becomes $\tau_R = \tau_s (N/N_s)^2$, where $N_s$ is the degree of polymerization between ion groups and $\tau_s$ is much higher than $\tau_0 N_s^2$ due to the delayed relaxation associated from the ionic interactons.\textsuperscript{121}

Recently, an analytical expression (Eq. 2.1) was introduced for the sticky Rouse model by Chen et al.\textsuperscript{76} to quantitatively predict the dynamic modulus of unentangled PEO ionomers.

$$G(t) = \sum_i \frac{\rho w_i R T}{M_i} \left\{ \sum_{p=N_{s,i}}^{N_i} \exp \left( -tp^2 / \tau_0 N_i^2 \right) + \sum_{p=1}^{N_{s,i}} \exp \left( -tp^2 / \tau_s N_{s,i}^2 \right) \right\}$$

(2.1)

Where $w_i$ is weight fraction of $i$th component with molecular weight of $M_i$, $N_i$ and $\tau_0$ are the number and the characteristic time of the elementary Rouse segment, which is usually comparable to the Kuhn segment, and $N_{s,i}$ is the number of strands between ionic groups for $i$th chain.\textsuperscript{76}

Eq. 2.1 can be divided into two parts. At scale shorter than the distance between ionic groups, the chain motion does not feel the constraints from the ionic interaction, thus the high order Rouse modes are the same with the nonionic polymers (the first part on the right side of Eq. 2.1). However, at larger scale of chain motion, the Rouse relaxation is restricted by the ionic interaction, and thus controlled by the association lifetime $\tau_s$. Therefore, the
low order Rouse modes are delayed (the second part on the right) by the ionic interaction.

The comparison of the master curves of PEO based ionomers with the prediction from sticky Rouse model (Eq. 2.1) is shown in Figure 2.16. The sticky Rouse model worked quite well for PEO ionomers with different ionic contents using only two parameters: the Rouse time of Kuhn segment $\tau_0$ and the ionic dissociation time (association lifetime) $\tau_s$, where $\tau_s$ was obtained separately from the dielectric relaxation time for $\alpha_2$ relaxation peak.\textsuperscript{76} This sticky Rouse model also worked for poly(tetramethylene oxide) (PTMO) based ionomers\textsuperscript{76} and phosphonium siloxane ionomers.\textsuperscript{122}

Figure 2.16 $G'$ and $G''$ master curves for Na-PEO600 ionomers having different ionic fractions as indicated at $T_r = 20^\circ$C. Solid lines show the prediction from sticky Rouse model. Reproduced from ref. 76, Copyright © 2013, The Society of Rheology.

2.3.6 Nonlinear viscoelasticity

In the polymer industry, polymers are often processed under high shear rates or high
deformation far beyond the linear region. Thus the understanding of nonlinear viscoelastic behavior, such as the steady shear and extensional behavior, is essential for the processing of ionomers. Typically, capillary rheometer or rotational rheometer with cone-plate geometry was used to measure the shear viscosity as a function of shear rate, where the latter one could give a more precise result owing to its constant shear rate throughout the testing region.

Typically, the ionomer melts exhibit Newtonian behavior at low shear rates, and then a shear thinning behavior at high shear rates. However, if the ionomer contains a relatively high ionic content or a strong ionic interaction, it might be difficult to detect the shear thinning region with the conventional rheometer due to its high melt viscosity. Recently, a shear thickening behavior, referred as the increase of steady state viscosity with increasing shear rate, was observed between the Newtonian region and the shear thinning region for oligomeric SPS4k ionomers (Figure 2.17). This shear thickening behavior was observed for Na and Li salts but not for K, Rb or Cs salts. The magnitude of shear thickening decreased with the increasing $T$ for both Na and Li salts, and was higher for the former because of its stronger ionic interaction. Although shear thickening has been widely investigated in the associative polymeric solution, it has been seldom observed in ionomer melts. The mechanism for this shear thickening behavior is still unknown, which might be related to the shear induced transition from intra-chain to inter-chain association.
The Cox-Merz rule, which states that the complex viscosity and shear viscosity are identical at low frequency or shear rate when the frequency $\omega$ equals to shear rate, is widely observed in non-associating polymers.\textsuperscript{124} However, the Cox-Merz rule is not applicable in many ionomer melts, such as PEMA and poly(styrene-co-n-butylmethacrylate) ionomers, because of their rheological complexity.\textsuperscript{79, 93, 125}

The elongational flow behavior of random ionomers has been studied for different ionomer systems, including polyesters\textsuperscript{126}, SPS\textsuperscript{80}, and PEMA\textsuperscript{68} ionomers. Connelly et al.\textsuperscript{126} investigated the effect of extensional rate and ionic content on the elongation viscosity of polyester ionomers. At short times, the elongational viscosity of polyester ionomers was almost same for different ionic contents, but at longer times the ionomer with higher ionic...
content exhibited higher elongational viscosity due to the stronger ionic interaction. The BKZ model worked quite well for non-ionic entangled polyesters, but failed for polyester based ionomers. In addition, the agreement with the BKZ model became even worse for ionomers with higher ionic content. In another study of partially neutralized entangled PEMA ionomers, the elongational viscosity of PEMA ionomers was well predicted by the BKZ model for both acid derivatives and metal salts, including Zn, Na, and Mg salts. The incorporation of metal cation increased both the linear and nonlinear elongational viscosity with Zn gave the highest viscosity followed by Na and Mg. The enhancement of the elongational viscosity was attributed to the stronger ionic interaction between metal carboxylate groups.

Recently, Ling et al. systematically investigated the effect of metal cation and temperature on the elongational viscosity of the oligomeric SPS ionomers. The elongational viscosity deviated from the linear viscoelastic envelop, and exhibited a weak strain hardening behavior (Figure 2.18). Although the SPS4k ionomers showed a well-defined plateau in the storage modulus similar to that of entangled PS, the ionomer broke up at relatively lower Hencky strain ($\varepsilon_H < 1$) than entangled PS because the brittle ionic network lacks the energy dissipation mechanism provided by the disentanglement of polymer chains.
The elongational flow of carboxylated telechelic polybutadiene ionomers (CPBD) with different alkali cations was studied by Stadler et al.\textsuperscript{127}. The authors found that the ionomer experienced a catastrophic failure at strain rate higher than the reciprocal of the terminal relaxation time due to the pulling out of the ionic groups from the ionic aggregates. In addition, strain hardening behavior occurred in the Li and Rb salts, but not in Na and K salts of CPBD ionomers. Similar with SPS ionomers, the Hencky strain at break is only 2-4, which is significantly lower than the value of ~8 for most polymers, indicating the brittleness of the ionic network.\textsuperscript{127}
CHAPTER III
LINEAR VISCOELASTICITY OF RANDOM OLIGOMERIC IONOMERS*

3.1 Introduction

It is well known that “gel” is a phenomenological term with diverse applications. Flory classified gels into four groups based on their structure: (1) Self-assembled gels with ordered structures, (2) covalently crosslinked disordered polymer gels, (3) disordered polymer gels formed by physical aggregation/association and (4) particulate disordered gels. The distinction between the chemical gels (class 2) and physical gels (class 3) is that the physical gel is thermally reversible and ultimately flows as a liquid while the chemical gel has permanent crosslinks. As a result, physical gels are similar to chemical gels in a certain time and temperature range where the physical aggregation/association is stable. Ionomers that form reversible gels are useful as hot melt adhesives. The gel point usually characterizes the liquid-to-solid transformation and network formation during the chemical crosslinking. As the gel point is approached, the large clusters percolate over the system, leading to divergence of the viscosity. The gel point is well defined for chemical crosslinking of long precursor chains, usually referred to as

vulcanization. Assume each precursor chain has \( f \) crosslinkable sites, the mean-field prediction of the gel point is: 
\[ p_c = \frac{1}{(f-1)} \]
In the previous study, we noted an analogous gel point for ionomer chains: Regarding each monomer of a styrene chain as a crosslinkable site via random sulfonation, the fraction of ionized (sulfonated) monomer \( p \) for a precursor chain having \( N \) monomers at the gel point is:
\[ p_c = \frac{1}{(N-1)\times100}\text{mol}\% \] (3.1)
corresponding to an average of one sulfonate per precursor chain. The relative extent of reaction is defined as:
\[ \varepsilon = \frac{(p - p_c)}{p_c} \] (3.2)

With \( \varepsilon < 0 \) below the gel point, \( \varepsilon = 0 \) at the gel point and \( \varepsilon > 0 \) beyond. The gel fraction \( P_{gel} \) is the order parameter of this connectivity transition, zero below the gel point, while above the gel point \( P_{gel} \sim \varepsilon \), which approaches 0 at the gel point, meaning the system is still occupied only by sol at the gel point, while fully occupied by gel at \( \varepsilon = 1 \) (\( p = 2p_c \)).

The gel point estimated by Eq. 3.1 is supported by the linear viscoelastic complex modulus reported by Weiss and coworkers. For random sulfonated oligomeric styrene with low molecular weight \( M = 4000\text{g/mol} \) (\( N = 38 \)) (< entanglement molecular weight \( M_e = 18000\text{g/mol} \)), the gel point is expected to be \( p_c = \frac{1}{(N-1)} = 2.7\text{mol}\% \). In accordance to this expectation, we found for ionomers having \( p = 2.5\text{mol}\% \) (\( \varepsilon = -0.064 \)), the terminal relaxation shows power law viscoelasticity usually seen quite close to the gel point. In comparison, the samples with \( p = 4.8\text{mol}\% \) (\( \varepsilon = 0.80 \)) and 6.5mol% (\( \varepsilon = 1.4 \)) exhibit a well-defined plateau before terminal relaxation, suggesting the samples are beyond the gel point.
and are reversible gels.

To better understand the sol-gel transition, examination was given on the linear viscoelasticity of these samples based on the mean-field theory of Rubinstein and Semenov. The theory predicts qualitatively the relaxation behavior. However, one apparent deviation is noted; the frequency dependence of storage modulus for the 2.5mol% sample exhibits power-law viscoelasticity but the power differs from that predicted by the mean-field theory. This difference encourages us to question the validity of the mean-field assumption.

In general, the mean-field theory is applicable when there is considerable overlapping of chains. At $p = 0$ and $\varepsilon = -1$, a precursor chain of $N$ segments and size $R \sim N^{1/2}$ has a self-concentration $\sim N/R^3 \sim N^{-1/2} < 1$ within its pervaded volume, meaning $N^{1/2}$ chains overlap in a pervaded volume in the melt. This number decreases as the gel point is approached and reaches unity at $-\varepsilon_G = -N^{1/3}$ known as the Ginzburg point, meaning clusters/strands are at their overlap concentration when $\varepsilon$ is close enough to the gel point, i.e. $-\varepsilon_G < \varepsilon < \varepsilon_G$, where critical percolation applies. A transition from mean-field to critical percolation can be seen if $N$ is neither too large, where mean-field percolation should dominate, nor too small, where critical percolation should dominate. In this study, we critically test this transition by changing the length of precursor PS chain $N$ and the extent of sulfonation $p$. We find strong evidence of this transition utilizing precursor PS chain having $M = 13500$ ($N = 130$) with ionic content very close to $p_c = 1/(N - 1) = 0.78$mol%. Since $M$ here is smaller than $M_c (= 18000g/mol)$, the number of chains in a
pervade volume is smaller than the threshold for entanglement. This number decreases with $p$ approaching $p_c$, meaning that the effect of entanglements are negligible even when average $M$ per cluster/strand becomes very large at $p$ close to $p_c$.

The mean-field theory of Rubinstein and Semenov is modified by including a critical percolation region for $-\varepsilon_G < \varepsilon < \varepsilon_G$. The modified theory can well predict the linear viscoelasticity of almost all the short lightly sulfonated styrene oligomers studied so far. In section 3.2, the necessary aspects of Rubinstein and Semenov’s model are reviewed and extended to include critical percolation close to the gel point. Section 3.3 provides experimental details and section 3.4 compares theory with experiment.

3.2 Reversible gelation theory

In this section we quickly review percolation theory for gelation, including mean-field theory and critical percolation closer to the gel point, as though all bonds are permanent. We then review Rubinstein and Semenov’s idea for effective breakup in mean-field and extend that to include critical percolation closer to the gel point.

3.2.1 Dynamics below the gel point

For samples below both the gel point and the Ginzburg point ($\varepsilon < -\varepsilon_G$), the molecular weight of the largest cluster $M_{\text{char}}$ increases with $\varepsilon$. The precursor chain has molecular weight $M_X = M_0 N_X$, size $R_X = N_X^{1/2} b$, and Rouse relaxation time $\tau_X = \tau_0 N_X^2$, with $b$ the segmental size, $N_X$ the number of segments, $M_0$ the segment molecular weight and $\tau_0$ the relaxation time of one segment. The mean-field theory gives the largest cluster having molecular weight $M_{\text{char}}$ and size $\xi_{\text{char}}$: 54
\begin{align*}
M_{\text{char}} &= M \left| \varepsilon \right|^2 \quad (3.3) \\
\varepsilon_{\text{char}} &= R_X \left( \frac{M_{\text{char}}}{M} \right)^{1/D} = R_X \left| \varepsilon \right|^{1/2} \quad (3.4)
\end{align*}

where $D (= 4$ in the mean-field gelation theory$^{130}$) is the fractal dimension so that the size of a cluster having molecular weight $M$ is $R/R_X = (M/M_X)^{1/D}$. Since the precursor chain is short, we may use the Rouse relaxation time,$^{136-138}$ $\tau_{\text{char}} \sim M_{\text{char}} \varepsilon_{\text{char}}^2 \sim M_{\text{char}}^{1+2/D}$ so that

\begin{align*}
\tau_{\text{char}} &= \tau_X \left( \frac{M_{\text{char}}}{M} \right)^{1+2/D} = \tau_X \left| \varepsilon \right|^{-3} \quad (3.5)
\end{align*}

The terminal relaxation modulus in this region is:

\begin{align*}
G \cong v k T \left| \varepsilon \right|^3 \quad (3.6)
\end{align*}

where $v$ is the number density of precursor chains. The mean-field theory holds until the Ginzburg point $\varepsilon_G = N_X^{-1/3}$, where the characteristic clusters no longer overlap and the mean-field scaling no longer holds, meaning that Eqs 3.3-3.6 hold only for $\varepsilon < -\varepsilon_G$.

The molecular weight, chain size, characteristic time, and terminal modulus of the cluster at the Ginzburg point can be obtained via inputting $\varepsilon_G = N_X^{-1/3}$ into Eqs 3.1-3.4 to obtain:$^{138}$

\begin{align*}
M_G &= M_X \varepsilon_G^{-2} = M_X N_X^{2/3} \quad (3.7) \\
\varepsilon_G &= R_X \left( \frac{M_G}{M_X} \right)^{1/D} = R_X N_X^{1/6} \quad (3.8) \\
\tau_G &= \tau_X \left( \frac{M_G}{M_X} \right)^{1+2/D} = \tau_X N_X \quad (3.9) \\
G &= v k T N_X^{-1} \quad (3.10)
\end{align*}

Further increasing $\varepsilon$ from $-\varepsilon_G$ ($-\varepsilon_G \leq \varepsilon < 0$) leads to critical percolation of Ginzburg blobs,$^{130,139,140}$
\[ M_{\text{char}} \cong M_G [\varepsilon / \varepsilon_G]^{-1/\sigma} = M_G [\varepsilon / \varepsilon_G]^{-2.2} \quad (3.11) \]
\[ \bar{\varepsilon}_{\text{char}} \cong \bar{\varepsilon}_G [\varepsilon / \varepsilon_G]^{-\nu} = \bar{\varepsilon}_G [\varepsilon / \varepsilon_G]^{-0.88} \quad (3.12) \]
\[ \tau_{\text{char}} \cong \tau_G [\varepsilon / \varepsilon_G]^{-2\nu-1/\sigma} = \tau_G [\varepsilon / \varepsilon_G]^{-4.0} \quad (3.13) \]
\[ G \cong G_G [\varepsilon / \varepsilon_G]^{(2\nu+1/\sigma)-0.67} = G_G [\varepsilon / \varepsilon_G]^{2.7} \quad (3.14) \]

For \( -\varepsilon_G < \varepsilon < 0 \), the relaxation time of the characteristic cluster increases with \( \varepsilon \) and diverges at the gel point (as \( \varepsilon \) approaches 0). In section 3.2.3 the relaxation time with reversible associations will be shown to have a maximum possible value set by effective breakup.

3.2.2 Dynamics above the gel point

In the following discussion, the \( 1 \leq \varepsilon \) case is first considered, where all chains are involved in the gel, secondly \( \varepsilon_G \leq \varepsilon < 1 \) where the system is mixture of sol and gel and mean-field percolation holds, thirdly \( 0 \leq \varepsilon < \varepsilon_G \) where the system is mixture of sol and gel and critical percolation holds.

At \( p \geq 2p_c \) (\( 1 \leq \varepsilon \)), all the chains are involved in the network whose modulus is proportional to the number-density of network strands. Considering that \( p_c \) corresponds to an average of one sticker per precursor chain, the number of ionic groups per precursor chain is \( p/p_c \), and the average number of network strands per precursor chain is \( N_s = p/p_c - 1 \equiv \varepsilon \). Replacing \( N_s \) with \( \varepsilon \) in the sticky Rouse model\(^76,^{121,141} \) predicting \( G \approx v_k T N_s \) and \( \tau_{\text{chain}} \approx \tau_s N_s^2 \),

\[ G = v_k T \varepsilon \quad \text{for } p \geq 2p_c \quad (3.15) \]
\[ \tau_{\text{chain}} \approx \tau_s \varepsilon^2 \quad \text{for } p \geq 2p_c \quad (3.16) \]
At $p = 2p_c$ and $\varepsilon = 1$, the plateau modulus recovers to the familiar result $G_N \approx v k T$ and relaxation time to the sticker lifetime $\tau_s$.

Above the Ginzburg point while below $\varepsilon \sim P_{gel} = 1$ ($\varepsilon_G \leq \varepsilon < 1$), the molecular weight of the network strand $M_{strand}$ decreases with increasing $\varepsilon$. The mean-field theory holds and the network strands have molecular weight, size, and characteristic Rouse time:

$$M_{strand} = M_X \varepsilon^{-2}$$

$$\xi_{strand} = R_X \left( \frac{M_{strand}}{M_X} \right)^{1/D} = R_X \varepsilon^{-1/2}$$

$$\tau_{strand} = \tau_X \left( \frac{M_{strand}}{M_X} \right)^{1+2/D} = \tau_X \varepsilon^{-3}$$

The plateau modulus in this mean-field percolation region is:

$$G \approx G_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^3 \approx v k T \varepsilon^3$$

The modulus recovers to $G_G$ at $\varepsilon_G$ and $v k T$ at $\varepsilon = 1$.

Below the Ginzburg point ($0 \leq \varepsilon < \varepsilon_G$), critical percolation holds, leading to formation of gel with strands of molecular weight, size, and Rouse time

$$M_{strand} \approx M_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-1/\sigma} = M_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-2.2}$$

$$\xi_{strand} \approx \xi_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-\nu} = \xi_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-0.88}$$

$$\tau_{strand} \approx \tau_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-2\nu-1/\sigma} = \tau_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{-4.0}$$

The plateau modulus of the gel in this region is:

$$G \approx G_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{(2\nu+1/\sigma)0.67} = G_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{2.7}$$

Equations 3.21-3.24 are perfectly symmetric with Eqs. 3.11-3.14 for $-\varepsilon_G < \varepsilon < 0$. The relaxation time of the reversible gel always relies on the effective breakup of strands. The symmetry between the structure of a gel strand at $\varepsilon > 0$ and that of a cluster at $\varepsilon < 0$ allows
an estimation of effective breakup time in both mean-field percolation and critical percolation regions, as explained next.

3.2.3 Effective Breakup

The discussion in sections 3.2.1 (below the gel point) and 3.2.2 (above the gel point) holds perfectly for permanent chemical bonds\textsuperscript{130, 137, 138} but reversible gels are always viscoelastic liquids and only act as permanent gels on time scales shorter than the sticker lifetime. On longer time scales both larger clusters and the reversible network relax by a pathway that Rubinstein and Semenov\textsuperscript{136, 137} term effective breakup, wherein large clusters (or gel strands) break into two smaller parts of comparable size. While the relaxation time of the characteristic cluster (Eqs 3.5 and 3.13) and the network strand (Eqs 3.19 and 3.23) get longer as the gel point is approached, the effective breakup time decreases as the gel point is approached, because more breakable sites are present in larger clusters/strands.

For mean-field percolation Rubinstein and Semenov\textsuperscript{136, 137} clearly discuss effective breakup, since intramolecular associations (loops) are not formed when clusters strongly overlap each other. Effective breakup refers to fragmentation of the backbone of the clusters, which results in two sub-clusters of comparable size and relaxation times much shorter than their mother cluster, Figure 3.1a\textsuperscript{136, 137}. In contrast, non-effective breakup occurs within the side branches of the cluster and result in a large cluster of similar size and relaxation time as the mother cluster and a small satellite cluster, Figure 3.1b. For critical percolation, however, there are loops and multiple backbones per cluster or strand.
For this case, the effective breakup sites are not so well defined.

![Diagram of a cluster with effective and non-effective breakups]

Figure 3.1 Dissociation of a cluster. (a) Effective breakup: breakup occurring at an ionic or dipolar association (purple circle) in the backbone (orange) and (b) non-effective breakup occurring at an association (green circle) involving a side branch (blue). All connections of the orange and blue lines represent associated ionic groups from different chains (strands).

The (orange) backbone of the mean-field percolation cluster or gel strand is a random walk of connected precursor chains with molecular weight

\[ M_{bb} = M_X \left( \frac{\xi_{\text{strand}}}{R_X} \right)^2 = M_X \epsilon^{-1} \]  

(3.25)

so there are \( M_{bb}/M_X = 1/\epsilon \) reversible bonds in this backbone that could break. The relaxation of the strand relies on effective breakup corresponding to lifetime:

\[ \tau_{\text{life}} = \tau_s M_X / M_{bb} = \tau_s \epsilon \]  

(3.26)

At the gel point (\( \epsilon = 0 \)) the lifetime is very short because the very long backbone has many reversible bonds that could break. This lifetime increases beyond the gel point and recovers to \( \tau_s \) at \( \epsilon = 1 \), where all precursor chains connect to the gel. The concept of
effective breakup, introduced by Rubinstein and Semenov, is where this lifetime (vanishing at the gel point, Eq 3.26) equals the Rouse relaxation time of the characteristic cluster (diverging at the gel point, Eq 3.5) or gel strand (Eq 3.19), corresponding to a critical extent of reaction $\varepsilon_c = (\tau_X/\tau_s)^{1/4}$ and the effective breakup relaxation time is obtained by substituting this critical extent of reaction into Eq 3.5, 3.19 or 3.26.

$$\tau_c = \tau_X^{1/4} \tau_s^{3/4}$$ (3.27)

Closer to the gel point than the critical extent of reaction $\varepsilon_c$, the gel strands and characteristic clusters are larger but they need to break to the same scale (with the same effective breakup time as Eq 3.27) in order to relax. At $\tau_c$, the characteristic modulus would be:

$$G_c = \frac{vkTNX^{3/4}}{\tau_s^{-3/4}}$$ (3.28)

This is the essence of Rubinstein and Semenov’s argument, which assumes $\varepsilon_c > \varepsilon_G$ so that this breakup acts on mean-field percolation clusters and strands. If, on the other hand, $\varepsilon_c < \varepsilon_G$, then the breakup acts on critical percolation clusters, whose statistics and dynamics have different scaling laws with extent of reaction, as partially discussed above.

Critical percolation forms loops in the orange backbone of Figure 3.1, complicating the derivation of $\tau_c$. Figure 3.10 will show that Eq 3.27 also holds for $\varepsilon_c < \varepsilon_G$. Then, the terminal modulus $G_c$ at effective breakup can be evaluated as:

$$G_c = G_G(\tau_X/\tau_c)^{0.67} = \frac{vkTNX^{-1/3}(\tau_X/\tau_s)^{0.5}}{}$$ (3.29)

For $\varepsilon_c \leq \varepsilon < \varepsilon_G$, $\tau_c = \tau_X^{1/4} \tau_s^{3/4}$ leads to the effective breakup time of a gel strand scaling
with plateau modulus $\tau_{\text{life}} \sim G^{1/2}$, as derived in the Appendix. Combining this scaling with Eq 3.24 and $\tau_{\text{life}} = \tau_s \varepsilon_G$ at $\varepsilon_G$ (Eq 3.26) gives:

$$\tau_{\text{life}} \cong \tau_s \varepsilon_G \left( \frac{\varepsilon}{\varepsilon_G} \right)^{1.35} = \tau_s N_X^{-1.35} \left( \frac{\varepsilon}{\varepsilon_G} \right)^{1.35}$$  \hspace{1cm} (3.30)

![Schematic illustration of terminal relaxation time and modulus](image)

Figure 3.2 Schematic illustration of (a) terminal relaxation time and (b) terminal relaxation modulus as functions of relative extent of sulfonation $\varepsilon$ in case of $\varepsilon_c < \varepsilon_G$.

Changes of (a) terminal relaxation time $\tau$ and (b) modulus $G$ with $\varepsilon$ are summarized in Figure 3.2, and the storage modulus against angular frequency $\omega$ is summarized in Figure 3.3: (1) For $-1 < \varepsilon < -\varepsilon_G$, clusters are formed via mean-field percolation and the relaxation
time relies on the Rouse relaxation having $\tau_{\text{char}} \sim |\epsilon|^{-3}$ (Eq 3.5, see Figure 3.2(a)) and $G \sim |\epsilon|^{-3}$ (Eq 3.6, see Figure 3.2b), leading to $G' \sim \omega$ (see Figure 3.3) before the terminal relaxation. (2) For $-\epsilon_{G} \leq \epsilon < -\epsilon_{c}$, critical percolation applies but the gel has not yet formed. The relaxation is still Rouse-type to give $\tau_{\text{char}} \sim |\epsilon|^{-4}$ (Eq 3.13, see Figure 3.2a), $G \sim |\epsilon|^{2.7}$ (Eq 3.14, see Figure 3.2b) and $G' \sim \omega^{0.67} (=2.7/4)$ (see Figure 3.3) before the terminal relaxation. The terminal relaxation time changes more significantly with $\epsilon$ than in region 1, because a more open structure is formed via critical percolation than via mean-field percolation. The exponent 0.67 is a signature of critical percolation.\textsuperscript{130, 139} (3) The relaxation time and effective breakup time coincide at $\epsilon_{c}$. Thus, in a region $-\epsilon_{c} \leq \epsilon < \epsilon_{c}$, the clusters/strands larger than those at $\epsilon_{c}$ have effective breakup time shorter than their intact Rouse relaxation time. Then, the effective breakup occurs continuously (before $\tau_{c}$) until the sub-clusters/strands reach a critical cluster/strand size, which then relax immediately (at $\tau_{c}$). Therefore, for $-\epsilon_{c} \leq \epsilon < \epsilon_{c}$, the relaxation time and modulus remain the same, i.e. $\tau_{c}$ (Eq 3.27, see Figure 3.2a) and $G_{c}$ (Eq 3.29, see Figure 3.2b). (4) For $\epsilon_{c} \leq \epsilon < \epsilon_{G}$, the gel starts to manifest as a plateau of $G'$, and the relaxation of gel strands is governed by effective breakup of clusters formed by critical percolation to give $\tau \sim |\epsilon|^{1.35}$ (Eq 3.30, see Figure 3.2a) and $G \sim |\epsilon|^{2.7}$ (Eq 3.24, see Figure 3.2b). In this region, the terminal relaxation modulus changes with terminal relaxation time as $G \sim \tau^{2}$ (see Figure 3.3). (5) For $\epsilon_{G} \leq \epsilon < 1$, the degree of gelation increases with $\epsilon$ and the system is still mixture of gel and sol to give plateau modulus smaller than $vkT$ ($G \approx vkT$ at $\epsilon = 1$) and the relaxation of gel strands is governed by effective breakup of mean-field percolation clusters with $\tau \sim \epsilon$ (Eq 3.26, see
Figure 3.2a) and $G \sim \varepsilon^3$ (Eq. 3.20, see Figure 3.2b). The terminal relaxation modulus changes with terminal relaxation time as $G \sim \tau^3$. (see Figure 3.3) Finally, for $\varepsilon > 1$, all the chains are involved in the gel to have plateau modulus larger than $\nu k T$ and increasing with $\varepsilon$. The strands between ionic groups become the gel strands, with $\tau \approx \tau_s \varepsilon^2$ (see Figure 3.2a) and $G \approx \nu k T \varepsilon$ (see Figure 3.2b), leading to sticky-Rouse type relaxation (see Figure 3.3).

![Figure 3.3](image_url) Schematic illustration of storage modulus $G'(\omega)$ during the gelation of reversible gels on logarithmic scales for $\varepsilon_c < \varepsilon < \varepsilon_G$. Terminal modulus and terminal relaxation ($G \sim \omega^2$) are highlighted in color for five cases: Orange is below the gel point at $\varepsilon = -\varepsilon_c$. Blue is close to the gel point with $-\varepsilon_c \leq \varepsilon < \varepsilon_c$ where the effective breakup keeps relaxation time constant. Green is above the gel point at $\varepsilon = \varepsilon_G$. Red is at $\varepsilon = 1$ where all sol clusters have attached to the gel. Purple is at $\varepsilon = 2$, further above the gel point. The dashed lines connecting terminal tails $-\varepsilon_c \leq \varepsilon < \varepsilon_c$ (blue), $\varepsilon_c \leq \varepsilon < \varepsilon_G$ (green), and $\varepsilon = 1$ indicate scaling of terminal relation modulus with terminal relaxation time in regions of $\varepsilon_c \leq \varepsilon < \varepsilon_G$ where $G \sim \tau_{\text{life}}^2$ and $\varepsilon_G \leq \varepsilon < 1$ where $G \sim \tau_{\text{life}}^3$.

3.2.3 Theoretical expression of complex modulus in terms of frequency

The theory in sections 3.2.1 and 3.2.2 is based on scaling. The frequency dependence
of complex modulus can be written as Eqs 3.31 to 3.36.

\[ G^*(\omega) = G^*_X(\omega) + G^*_MF(\omega) \]

\[ = i\omega v k T \left[ \sum_{n=2}^{N_x} \frac{\tau_X/n^2}{1 + i\omega \tau_X/n^2} + \int_{\tau_X}^{\infty} \frac{(\tau_X/\tau)^{1/2}}{i\omega + 1/\tau_{char} + 1/\tau} \, d\tau \right] \quad (\varepsilon < -\varepsilon_G) \quad (3.31) \]

For \( \varepsilon < -\varepsilon_G \), the cluster is formed by mean-field percolation and thus the complex modulus has contributions from the Rouse relaxation of the precursor chains (subscript “X”) and Rouse relaxation of mean-field percolation clusters (subscript “MF”). The Rouse relaxation of the precursor chains ends at the second mode \( (p = 2) \) simply because the first mode has been readily incorporated in the MF term. For MF part, the relaxations start at \( \tau_X \) and ends at \( \tau_{char} \), and \( G^*(\omega) \sim (i\omega)^u \) with \( u = 1 \). Considering these conditions, the MF part of the modulus can be written as integration of \( (\tau_{startup}/\tau)^u/[i\omega + 1/\tau_{cutoff} + 1/\tau] \) in Eq 3.31, where integrand \( (\tau_{startup}/\tau)^u/[i\omega + 1/\tau_{cutoff} + 1/\tau] \) is commonly written for both mean-field and critical percolation parts in Eqs 3.32-3.35.

\[ G^*(\omega) = G^*_X(\omega) + G^*_MF(\omega) + G^*_CP(\omega) \]

\[ = i\omega v k T \left[ \sum_{n=2}^{N_x} \frac{\tau_X/n^2}{1 + i\omega \tau_X/n^2} + \frac{N_x - 1}{N_x} \int_{\tau_X}^{\infty} \frac{(\tau_X/\tau)^{1/2}}{i\omega + 1/\tau_{G} + 1/\tau} \, d\tau + \frac{0.67}{N_x} \int_{\tau_G}^{\infty} \frac{(\tau_{G}/\tau)^{0.67}}{i\omega + 1/\tau_{char} + 1/\tau} \, d\tau \right] \quad (-\varepsilon_G \leq \varepsilon < -\varepsilon_c) \quad (3.32) \]

For \( -\varepsilon_G \leq \varepsilon \leq -\varepsilon_c \), mean-field and critical percolation govern on length scales smaller and larger than \( \xi_G \), respectively. Then, the complex modulus has contributions from (1) Rouse relaxation of the precursor chain (2) Rouse relaxation of the sub-cluster formed from mean-field percolation and (3) Rouse relaxation from MF subcluster to the whole cluster formed from critical percolation (subscript “CP”).
\[
G^*(\omega) = G_X^*(\omega) + G_{MF}^*(\omega) + G_{CP}^*(\omega)
\]

\[
i\omega v T \left[ \sum_{n=1}^{N} \frac{\tau_x/n^2}{1+i\omega \tau_x/n^2} + \frac{N_x-1}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/\tau + 1/\tau} \right] + \frac{0.67}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/(\lambda \tau_c) + 1/\tau}
\]

\[-\epsilon_c \leq \epsilon < \epsilon_c\] (3.33)

For \(-\epsilon_c \leq \epsilon < \epsilon_c\), the only difference from Eq 3.32 is the cutoff frequency is \(\lambda \tau_c\) for the CP part, with \(\tau_c = \tau_x^{0.25} \tau_s^{0.75}\) (Eq 3.27) the characteristic time of critical cluster. Here, \(\lambda\) is a fitting parameter of order unity. Introduction of this prefactor is reasonable considering \(\tau_c\) is obtained based on scaling argument.

\[
G^*(\omega) = G_X^*(\omega) + G_{MF}^*(\omega) + G_{CP}^*(\omega) + G_{N}^*
\]

\[
i\omega v T \left[ \sum_{n=1}^{N} \frac{\tau_x/n^2}{1+i\omega \tau_x/n^2} + \frac{N_x-1}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/\tau + 1/\tau} \right] + \frac{0.67}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/(\lambda \tau_c) + 1/\tau}
\]

\[-\epsilon_G \leq \epsilon < \epsilon_G\] (3.34)

For \(-\epsilon_c \leq \epsilon < \epsilon_G\), the complex modulus has contributions from (1) the Rouse relaxation of precursor chain, (2) the Rouse relaxation of sub-strand formed by mean field percolation (3) the Rouse relaxation from MF sub-strand to strand formed by critical percolation, with \(1/\tau_{strand}\) the characteristic frequency of a strand, and (4) a gel plateau with amplitude given by Eq 3.24 that relaxes at relaxation time \(\tau_{life}\) given by Eq 3.30.

\[
G^*(\omega) = G_X^*(\omega) + G_{MF}^*(\omega) + G_{N}^*
\]

\[
i\omega v T \left[ \sum_{n=1}^{N} \frac{\tau_x/n^2}{1+i\omega \tau_x/n^2} + \frac{N_x-1}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/\tau + 1/\tau} \right] + \frac{0.67}{N_x} \int_{\tau_x}^{\infty} \frac{d\tau}{i\omega + 1/(\lambda \tau_c) + 1/\tau}
\]

\[-\epsilon_G \leq \epsilon < 1\] (3.35)

For \(-\epsilon_G \leq \epsilon < 1\), the modulus has contributions from (1) the Rouse relaxation of
precursor chains, (2) the Rouse relaxation of strand formed by mean field percolation (3) a
gel plateau with amplitude given by Eq 3.20 that relaxes at relaxation time $\tau_{\text{life}}$ given by Eq

$$G^* (\omega) = G_X^* (\omega) + G_{SR}^* (\omega) = i \omega v k T \left[ \sum_{n=1}^{N_X} \frac{\tau_X / n^2}{1 + i \omega \tau_X / n^2} + \sum_{n=1}^{\varepsilon} \frac{\tau_X \varepsilon^2 / n^2}{1 + i \omega \tau_X \varepsilon^2 / n^2} \right] \quad (1 \leq \varepsilon) \quad (3.36)$$

For $1 \leq \varepsilon$, the modulus is given by the sticky Rouse model. Since the number of
sticky Rouse segments per chain $\sim \varepsilon$, the complex modulus is written as a combination of
high order Rouse modes with $N_X \geq p > \varepsilon$ with Rouse time $\tau_X$ and low order sticky Rouse
modes (subscript “SR”) with $\varepsilon \geq p \geq 1$ that are delayed by ion associations with lifetime $\tau_s$.

3.3 Experimental section

This section described the synthesis of SPS ionomers and the characterization of the
rheological behavior of SPS ionomers.

3.3.1 Materials

Two narrow molecular weight polystyrenes, PS4.6 with $M_w = 4,600$ Da and PS13.5
with $M_w = 13,500$ Da, were obtained from Pressure Chemical Co. and sulfonated in
dichloroethane (DCE) using acetyl sulfate. The homogeneous solution sulfonation
produces random substitution of sulfonic acid group at the para-position of the phenyl
ring. The acetyl sulfate was prepared by slowly adding concentrated sulfuric acid to a
60% excess of acetic anhydride in 1,2-dichloroethane at 0 °C. The freshly prepared acetyl
sulfate was added to a stirred 10% solution of PS in DCE at ~50 °C. The reaction was
terminated after 1 h by the addition of 2-propanol. The SPS was isolated by steam

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distillation of the solvent, washed three times with boiling water, dried in air at 70 °C for 1 day, and finally dried at 120 °C in a vacuum oven for 1 week. The sulfonation level was determined by elemental sulfur analysis Galbraith Laboratories, Inc.

Four sulfonation levels were prepared for SPS4.6, 1.0, 1.6, 2.5 and 2.8mol % and there were six sulfonation levels for the SPS13.5, 0.066, 0.20, 0.52, 0.76, 1.2 and 2.7 mol%. The average number of ionic groups per chain was designed to be 0.4, 0.7, 1.1 and 1.2 for the four SPS4.6 ionomers, and 0.1, 0.3, 0.7, 1, 1.6 and 3.5 for the SPS13.5, though since sulfonation proceeds randomly the products included a random distribution of chains with varying sulfonation. Alkali metal salts of SPS were prepared by adding a 50% excess of the appropriate metal hydroxide or acetate to the SPS acid derivative in a 90/10 (v/v) mixture of toluene and methanol. The neutralized ionomer was recovered by steam distillation and washed and dried. The sample nomenclature is MSPSx-p, where x =4.6 or 13.5 is the molecular weight of PS precursors, and p is the degree of sulfonation in mol%.

3.3.2 Materials characterization

Linear viscoelasticity (LVE) measurements were conducted on either a TA Instruments Advanced Rheological Expansion System (ARES-G2) rheometer. Parallel plate fixtures of 25 and 8 mm were used for LVE measurements in a T range of 80 to 250°C and a frequency range of 0.01 to 63Hz. All measurements were made within the linear regime as confirmed from strain sweep experiments. Master curves for the PS4.6, PS13.5, SPS4.6, and SPS13.5 ionomers were constructed at the same reference temperatures of $T_r = 140^\circ$C for comparison.
3.4 Results and discussion

This section discussed the effect of sulfonation degree and metal cation on the rheological behavior and compared the experimental data with the model predictions.

3.4.1 Neat ionomers

Figures 3.4a and 3.4b show the master curves of storage and loss modulus at $T_r = 140^\circ\text{C}$ for NaSPS13.5 and NaSPS4.6 with ionic contents ranging from $p << p_c$ ($\varepsilon < 0$), to $p \sim p_c$ ($\varepsilon \sim 0$), and $p > p_c$ ($\varepsilon > 0$), respectively.

For both SPS13.5 and SPS4.6 ionomers, a plateau in $G'$ was not observed when $p < p_c$. For $p \sim p_c$, both NaSPS13.5-0.76 and NaSPS4.6-2.5 ionomers show power law like relaxation before the terminal relaxation time, suggesting the gel has not yet been well formed. In particular, NaSPS4.6-2.5 ionomer exhibits a very weak plateau in $G'$ because of its slightly higher ionic content than the gel point ($\varepsilon = 0.08 > 0$). Whereas ionomers with $p > p_c$ show clear plateau corresponding to the gel structure. Furthermore, the plateau modulus increased with increasing ionic content $p$ due to the increasing density of effective crosslinking. This result supports the gel point estimated via Eq 3.1, $p_c = 2.3\text{mol}\%$ for PS4.6 and $p_c = 0.78\text{mol}\%$ for PS13.5 are reasonable.

Figure 3.5a, 3.5b, and 3.5c show master curves of storage and loss modulus at $T_r = 140^\circ\text{C}$ for SPS13.5 ionomers with ionic contents of 0.76mol\% ($\varepsilon = -0.026$) and 2.7mol\% ($\varepsilon = 2.5$), and SPS4.6 ionomers with ionic content of 2.5mol\% ($\varepsilon = 0.08$), respectively.
Figure 3.4 Frequency dependence of storage and loss moduli, $G'$ and $G''$, master curves at $T_r = 140 \, ^\circ C$ for (a) NaSPS13.5, and (b) NaSPS4.6 ionomers. The solid lines are the model predictions.
Figure 3.5 Frequency dependence of storage and loss moduli, $G'$ and $G''$, master curves at $T_r = 140$ °C for (a) SPS13.5-0.76, (b) SPS13.5-2.7 and (c) SPS4.6-2.5 ionomers. The solid lines are model predictions.
For each ionic content, $G'$ and $G''$ are compared for ionomers having various alkali counterions: Sodium (Na), Potassium (K), Rubidium (Rb), and Cesium (Cs). It is noted that the relaxation time increases with decreasing the counterion size. The trend is in accordance with a simple expectation that the lifetime of ionic association increases with ionic interaction energy, which increases when the size of ion decreases. It is obvious the relaxation behavior is quite different for SPS4.6-2.5 and SPS13.5-0.76 samples compared with SPS13.5-2.7 samples (Figure 3.5): for every cation, both SPS4.6-2.5 and SPS13.5-0.76 ionomers show power law like relaxation over a very wide range of frequency, indicating the existence of characteristic structure, whereas SPS13.5-0.27 ionomers show a clear plateau in $G'$ similar to that of entangled polymers.

In particular, for the SPS13.5-0.76 ionomers, the storage modulus is plotted against $\omega$ in Figure 3.6, where three power law regions can be observed from high to low frequency: (1) the Rouse region where $G'(\omega) \sim \omega^{1/2}$, (2) the mean-field gelation region where $G'(\omega) \sim \omega^1$, and (3) the critical percolation region where $G'(\omega) \sim \omega^{0.67}$, followed by the terminal relaxation $G'(\omega) \sim \omega^2$. Similar power law relaxation can also be observed in SPS4.6-2.5 ionomers despite the occurrence of a very weak plateau. These results rationalizes our incorporation of the Ginzburg point in section 3.2.
Figure 3.6 Frequency dependence of storage modulus $G'$ master curves at $T_r = 140 \, ^\circ C$ for SPS13.5-0.76 ionomers. The thin solid lines above the curve shows the power law regions (1) $G' \propto \omega^{0.5}$, (2) $G' \propto \omega^1$, and (3) $G' \propto \omega^{0.67}$ before terminal relaxation region $G'' \propto \omega^2$.

Before detailed discussion of the master curves, a comment is needed on the time temperature superposition (TTS) utilized to construct the master curves. It should be noted that the TTS works quite well for ionomers with $p < p_c$, but fails when $p \sim p_c$ or $p > p_c$. Specifically, TTS fails in the terminal region of $G'$ for NaSPS13.5-0.76 where $p \sim p_c$ and in the valley preceding the terminal region of $G''$ for the ionomers with $p > p_c$ (NaSPS13.5-1.2, SPS13.5-2.7, and NaSPS4.6-2.8 ionomers), see Figures 3.4 and 3.5. In particular, TTS fails in the valley region of $G''$ for SPS4.6-2.5 ionomers ($p \sim p_c$) rather than the terminal region probably due to its ionic content slightly higher than the gel point. The failure of TTS is due to two relaxation processes$^{71}$, characterized by the Rouse relaxation time $\tau_r$. 

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(relaxation time of precursor chain), and the ionic dissociation time $\tau_s$, that have different temperature dependences. The terminal relaxation of the ionomer near the gel point ($p \sim p_c$) is governed by the effective breakup of the clusters into smaller clusters of comparable size, where the effective breakup time $^{136, 137}$ is $\tau_c \sim \tau_x \tau_s^{3/4}$, where $\tau_x$ is the Rouse relaxation time for the chain. The thermorheological complexity of SPS13.5-0.76 can be attributed to the different temperature dependences of Rouse relaxation at high frequency and effective breakup in the terminal region. For $p > p_c$, TTS fails in the frequency region near the minimum in $G''$, where two relaxation mechanisms, Rouse relaxation and ionic dissociation, overlap.

Figures 3.7 and 3.8 show the temperature dependence of the shift factors used to obtain the master curves in Figures 3.4 and 3.5, respectively. Those WLF constants used to fit the shift factors are summarized in Tables 3.1 and 3.2. For each ionic content, the cation has little effect on the temperature dependence of shift factors (Figure 3.5 and Table 3.2). While for both NaSPS13.5 and NaSPS4.6 ionomers, the shift factors is strongly affected by the change of ionic content $p$. When $p < p_c$, the shift factors of ionomers can be described using almost the same WLF constants for the PS precursors, see Figure 3.7 and Table 3.1. For $p \sim p_c$, the WLF constants used for the fitting began to deviate from that of PS precursors (Table 3.1). In general, both $C_1$ and $C_2$ increased with increasing ionic content $p$ for both NaSPS13.5-$p$ and NaSPS4.6-$p$ ionomers. The free volume theory predicts that those WLF constants follow the relations of $C_1 \propto 1/f_f$ and $C_2 \propto f_f/\alpha_f$ with $f_f$ as the fractional free volume at $T_r$ and $\alpha_f$ as the free volume expansion coefficient. $^{71}$ The increasing $C_1$ and
$C_2$ indicates both fractional free volume and volume expansion coefficient decrease with increasing $p$ due to the densification of ionomer chains. It should be noted that the shift factors at higher temperatures decrease with $p$, and the WLF fitting becomes worse. This stronger temperature dependence of shift factor was reported previously as being due to a stronger $T$ dependence of $\tau_s$ compared with that of $\tau_0$.\textsuperscript{76}

Figure 3.7 Time-temperature shift factor $a_T$ for NaSPS13.5-$p$ and NaSPS4.6-$p$ ionomers with $T_r = 140^\circ$C. The shift factors of NaSPS4.6-$p$ ionomers were multiplied by 100 for clarity. The solid lines show the WLF fits.
Figure 3.8 Time-temperature shift factor $a_T$ for (a) SPS13.5-0.76 and SPS13.5-2.7, and (b) SPS4.6-2.5 ionomers with $T_r = 140^\circ$C. The solid lines show the WLF fits.
Table 3.1 WLF Constants for NaSPS13.5 and NaSPS4.6 ionomers

<table>
<thead>
<tr>
<th></th>
<th>PS13.5</th>
<th>NaSPS13.5-p</th>
<th>NaSPS4.6-p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.066</td>
<td>0.20</td>
</tr>
<tr>
<td>C1</td>
<td>7.5</td>
<td>7.7</td>
<td>7.3</td>
</tr>
<tr>
<td>C2(K)</td>
<td>106</td>
<td>107</td>
<td>100</td>
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Table 3.2 WLF Constants for SPS13.5-0.76, SPS13.5-2.7 and SPS4.6-2.5 ionomers

<table>
<thead>
<tr>
<th></th>
<th>SPS13.5-0.76</th>
<th>SPS13.5-2.7</th>
<th>SPS4.6-2.5</th>
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<tbody>
<tr>
<td></td>
<td>Na</td>
<td>K</td>
<td>Cs</td>
</tr>
<tr>
<td>C1</td>
<td>7.8</td>
<td>8.0</td>
<td>8.2</td>
</tr>
<tr>
<td>C2(K)</td>
<td>103</td>
<td>104</td>
<td>106</td>
</tr>
</tbody>
</table>

3.4.2 Comparison with the model predictions

To quantitatively test the relaxation mechanism, Figures 3.4 and 3.5 compare the model prediction and experimental results of all sets of samples having different ionic contents and metal cations. The reversible gelation model fits the $G''$ data well for $p < p_c$. 

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but under-predicts $G'$ in the lower frequency range. The discrepancy in $G'$ may be due to the failure of the model to consider a molecular weight distribution and the assumption that only the effective breakup of the backbone influenced the relaxation of the cluster. Non-effective breakup of the side-chain branches may also produce higher frequency relaxations that would broaden the overall relaxation of the clusters and is expected to be more pronounced for the higher sulfonated ionomer. That explanation is consistent with the greater deviation observed for the experimental data and model predictions for NaSPS13.5-0.52 and NaSPS4.6-1.6 than for NaSPS13.5-0.20, NaSPS13.5-0.066 and NaSPS4.6-1.0.

For $p \sim p_c$ (SPS13.5-0.76 and SPS4.6-2.5), the LVE behavior showed two distinct power law regions before terminal relaxation, mean-field behavior ($G' \sim G'' \sim \omega^1$) at higher frequencies, followed by critical percolation behavior ($G' \sim G'' \sim \omega^{2/3}$), which is consistent with the model prediction. When $p > p_c$ (NaSPS13.5-1.2, SPS13.5-2.7, and NaSPS4.6-2.8), the model predictions agree well with the terminal relaxation but over- or under-predict the plateau modulus. For SPS13.5-2.7 ionomers ($p > 2p_c$), where the system is completely gelled, the model over-predicted $G_N$, which is probably a consequence of the model assumption that all strands (i.e., the chain between sulfonate groups) are stress-bearing. That is not the case because defects in the network, e.g., dangling ends, loops or unassociated (isolated) ionic groups do not support stress. However, the model under predicts $G_N$ for NaSPS4.6-2.8. The reason for this phenomenon is unknown, which might be related to the underestimation of the ionic content $p$. Since a small variation of $p$ could significantly alter the plateau modulus especially when $p_c < p < 2p_c$. 

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Table 3.3 Rouse relaxation time (\(\tau_0\)) and ionic dissociation time (\(\tau_s\)) used for NaSPS13.5-p, SPS13.5-0.76, and SPS13.5-2.7 ionomers at 140°C

<table>
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<tr>
<th></th>
<th>PS13.5</th>
<th>NaSPS13.5-p</th>
<th>SPS13.5-0.76</th>
<th>SPS13.5-2.7</th>
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</thead>
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<tr>
<td>(\tau_0) ((\mu s))</td>
<td>20</td>
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<td>27</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>52</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>(\tau_0) ((\mu s))</td>
<td>96</td>
<td>6</td>
<td>0.2</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>463</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\tau_s) (s)</td>
<td>3300</td>
<td>4340</td>
<td>4650</td>
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</tr>
</tbody>
</table>

Table 3.4 Rouse relaxation time (\(\tau_0\)) and ionic dissociation time (\(\tau_s\)) used for NaSPS4.6-p, and SPS4.6-2.5 ionomers at 140°C

<table>
<thead>
<tr>
<th></th>
<th>SPS4.6-1.0</th>
<th>SPS4.6-1.6</th>
<th>SPS4.6-2.5</th>
<th>SPS4.6-2.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau_0) ((\mu s))</td>
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<td>1.3</td>
<td>3.8</td>
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<tr>
<td></td>
<td>6.6</td>
<td>6.5</td>
<td>6.5</td>
<td>6.7</td>
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<tr>
<td>(\tau_0) ((\mu s))</td>
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</tr>
<tr>
<td>(\tau_s) (s)</td>
<td>2500</td>
<td>450</td>
<td>250</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>5000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tables 3.3 and 3.4 summarize the values of the Rouse relaxation time of an Kuhn segment (\(\tau_0\)) and the ionic dissociation time (\(\tau_s\)) obtained from nonlinear least-squares fit of dynamic moduli shown in Figures 3.4 and 3.5 (solid curves). For NaSPS13.5-p and
NaSPS4.6-p ionomers, the $\tau_0$, which is higher than that of the PS bulk, as obtained from fitting the PS data to the Rouse model, increases with the sulfonation degree $p$, presumably due to the increased fraction of segments whose mobility is restricted by the ionic interactions. As shown in Figure 3.9, a linear relation between $\tau_0$ and ionic content $p$ can be obtained for both SPS13.5 and SPS4.6 ionomers. This increasing dependence of $\tau_0$ is consistent with the increase of dynamic modulus in the Rouse region ($G' \sim G'' \sim \omega^{1/2}$) at frequency higher than the mean field region for ionomers with higher $p$ (see Figure 3.4). $\tau_s$ for NaSPS13.5- and NaSPS4.6-p ionomers, also increases with $p$, which may be a consequence of better packing of the ionic associations at the higher sulfonation levels. Decreasing $E_c$ (i.e., increasing the cation radius) has only small effect on $\tau_0$ for the SPS13.5-0.76, SPS13.5-2.7, and SPS4.6-2.5 ionomers, but it significantly reduces $\tau_s$. The increase of cation size from Na to Cs decreases $\tau_s$ by 2 orders of magnitude. Compared to SPS13.5 ionomers, $\tau_0$ is much lower for SPS4.6 ionomers probably due to their much lower glass transition temperature, while $\tau_s$ is almost independent of the molecular weight of the PS precursors.
Figure 3.9 Relation between $\tau_0$ and $p$ for SPS13.5 and SPS4.6 ionomers with each point denotes one sample. The black and red solid line shows the linear fit with equation $\log \tau_0 (\mu s) = 1.3 + 0.49p$, and $\log \tau_0 (\mu s) = -0.062 + 0.38p$, respectively.

Since $p = 2.5\text{mol}\%$ of the SPS4.6 samples and $p = 0.76\text{mol}\%$ of SPS13.5 ionomers are very close to their gel points $p_c = 2.3\text{mol}\%$ and $0.78\text{mol}\%$, respectively, their terminal relaxations likely occur by effective breakup. These two samples correspond to $-\varepsilon_c \leq \varepsilon < 0$, where clusters relax by Rouse motion until effective breakup at $\tau_c$. This expectation can be tested quantitatively via $\tau_c \propto \tau_x^{1/4} \tau_s^{3/4}$ (Eq. 3.27). On one hand, $\tau_x$ and $\tau_s$ can be determined from the nonlinear fitting, on the other hand, $\tau_c$ can be estimated from the terminal region. In Figure 3.10, $\tau_c$ ($\tau$ of SPS4.6 of 2.5 mol\% and SPS13.5 of 0.76 mol\%) is plotted against $\tau_x^{0.25} \tau_s^{0.75}$, with each point corresponding to one counterion. The proportionality is well observed, which supports the relaxation by effective breakup.
assigned for the SPS4.6 of 2.5mol% and SPS13.5 of 0.76mol% samples close to their gel points.

![Graph](image)

Figure 3.10 Test of effective breakup time for SPS4.6-2.5 and SPS13.5-0.76 ionomers (Eq 3.27). \( \tau_X \) is the relaxation time of the precursor chain. \( \tau_s \) is the ionic dissociation time. Both \( \tau_X \) and \( \tau_s \) were determined from the model fitting. \( \tau_c \) is estimated as the terminal relaxation time. Solid line is linear fit with \( \tau_c = 0.94 \tau_s^{3/4} \tau_s^{1/4} \).

3.5 Conclusions

Using standard percolation theory for gelation that includes both critical and mean-field regimes, the linear viscoelastic response of lightly sulfonated short polystyrene is quantitatively understood. LVE behavior changes drastically in the vicinity of the gel point, corresponding to an average of one crosslink per chain. Very close to the gel point the
effective breakup ideas of Rubinstein and Semenov appear to control the terminal relaxation. The association lifetime and energy both are found to increase logically as counterions get smaller.

To our best knowledge, this work is the first precise control of sulfonated polystyrene close to the gel point where $p \sim p_c \sim 1/(N−1)$ corresponding to one ionic group per chain on average. Most of the previously studied sulfonated polystyrene samples have $p$ much higher than $p_c$ are not suitable to test the sol-gel transition.\textsuperscript{56, 121, 143, 144} These samples show typical reversible gel behavior characterized by clear plateaus and delayed relaxation governed by the dissociation time $\tau_s$.
CHAPTER IV
LINEAR VISCOELASTICITY OF OLIGOMERIC SULFONATED POLYSTYRENE
IONOMER BLENDS*

4.1 Introduction

Ionomers are predominantly non-polar polymers containing a small amount of covalently attached ionic groups. The polar ionic groups tend to form nanometer-sized ionic aggregates in non-polar media due to strong intermolecular ionic or dipolar associations that behave as reversible crosslinks. These intermolecular interactions and the supramolecular microstructure are responsible for the excellent physical and mechanical properties of ionomers, which have produced significant academic and industrial interest for nearly six decades\textsuperscript{145}. Ionomers have applications in a variety of technologies, such as membranes\textsuperscript{146}, thermoplastic elastomers, compatibilizers for polymer blends\textsuperscript{147}, and more recently as shape memory polymers and self-healing materials\textsuperscript{145}.

Polymer blending is an economical and efficient method for developing new polymeric materials with properties that are not easily achieved with a single polymer\textsuperscript{148}. For example, blends of two different ionomers, a zinc salt and a sodium salt of poly(ethyl-
ene-co-methacrylic acid), Zn-PEMA and Na-PEMA, possess a unique combination of elasticity and toughness\textsuperscript{149} that makes them suitable for the cover of golf balls. Although there is extensive literature concerning blends of neutral polymers with ionomers, there has been little published research on blends of different ionomers except for a limited literature on blends of two different salts of PEMA (or poly(ethylene-co-acrylic acid))\textsuperscript{149-152}, which are used in golf ball applications.

The general subject of ionomer dynamics and melt rheology was reviewed by Register and Prud’homme\textsuperscript{153}. With the exception of a 2005 paper by Nishio et al.\textsuperscript{70}, there have been no published studies concerned with the dynamics of ionomer blends. Nishio et al.\textsuperscript{70} reported that time-temperature-superposition (TTS) was obeyed by the linear viscoelastic (LVE) properties of the blends and the zero shear viscosity of PEMA ionomer blends was generally lower than expected due to effects of the residual, non-neutralized, carboxylic acid groups that are present in PEMA ionomers.

The results of Nishio et al.\textsuperscript{70} emphasizes a significant problem with generalizing rheology results for PEMA (or PEAA) ionomers is that they are not fully neutralized. They are actually terpolymers of ethylene, methacrylic acid (or acrylic acid) and a metal methacrylate (or acrylate). Although it is a weaker interaction than the ionic and dipolar interactions, hydrogen bonding of the acid groups complicates the answer to the question of how the ionic groups affect the dynamic response. In addition, carboxylic acid component can also plasticize or solvate the ionic or dipole-dipole interactions of the salt groups, which weakens the effect of the interactions of the ionic species\textsuperscript{100}.

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With sulfonate ionomers, it is easier to achieve complete neutralization of the acid groups, because of the much lower pK$_a$ of the sulfonic acid (~1.0) compared with pK$_a$ of carboxylic acids (~4 - 5). The viscosities and relaxation times of sulfonate ionomers are also orders of magnitude greater than carboxylate ionomers even when the latter is fully neutralized$^{20}$. In addition, for high molecular weight ionomers, the influence of trapped entanglements can be significant and even comparable to the ionic interactions, which obfuscates the specific effects of the ionic species.

Randomly sulfonated polystyrene oligomers (SPS) have recently been used to isolate the effects of the ionic groups on the rheology of ionomers, specifically the effects of the ionic concentration and the choice of cation on the shear and extensional dynamics of ionomer melts$^{32, 80, 85, 154, 155}$. The use of oligomers precludes any effects of chain entanglements on the rheology. The *gel point* of neat ionomers occurs at one ionic group per chain on average, and two power law regions are observed in their LVE response, with scaling behaviors typical of mean-field and critical percolation$^{154}$. Above the gel point, a supramolecular network (gel) is formed, as evident from a plateau observed in the storage modulus that is independent of cation$^{32, 80, 154}$. The relaxation time of the ionomers increases with decreasing cation size$^{32}$, which for alkali metal cations corresponds to increasing Coulomb energy of the ion-pair.

A reversible gelation model for the ionomer dynamics was developed$^{154}$ based on the mean-field theory of Rubinstein and Semenov$^{136, 137}$ by incorporating a transition from mean-field to critical percolation at the Ginzburg point$^{156}$. The LVE behavior of SPS
samples with different cations and ionic concentration agreed well with this reversible
gelation model, which requires only two inputs, the Rouse time of a Kuhn segment, \( \tau_0 \), and
the ionic dissociation time, \( \tau_s \).154

In the chapter, the validity of the reversible gelation model is discussed for the binary
blends of oligomeric SPS ionomers using different cations and ionic concentrations. A
simple mixing rule is proposed for using the reversible gelation model to estimate the LVE
response of ionomer blends.

4.2 Experimental section

This section described the synthesis of SPS ionomers and the characterization of the
rheological behavior of SPS ionomers.

4.2.1 Materials

Oligomeric polystyrene (PS13.5) with \( M_w = 13.5 \text{ kg/mol} \) and a polydispersity index
(PDI) of 1.06 was obtained from Pressure Chemical Co. (Pittsburgh, PA). The sulfonation
of PS was carried out in a 1,2-dichloroethane (DCE) solution with acetyl sulfate following
the procedure of Makowski et al.14. Acetyl sulfate was prepared through the reaction of
concentrated sulfuric acid and a 60 mol% excess of acetic anhydride in DCE at 0°C. The
freshly prepared acetyl sulfate was added to a ~10 wt% PS/DCE solution over a period of
~1 min at ~50°C with continuous stirring. After 1 h the reaction was terminated by adding
~2 ml 2-propanol. The sulfonation reaction is an electrophilic substitution reaction that
occurs primarily at the para-position of the phenyl ring157. The sulfonation product, the
sulfonic acid derivative of sulfonated polystyrene (SPS13.5), was precipitated in boiling
deionized water, washed three times with deionized water, dried in air at 70°C for 1 day
and finally dried at 120°C in a vacuum oven for 1 week. The sulfonation level was
determined by sulfur elemental analysis at Robertson Microlit Analysis (Madison, NJ).
This sulfonation procedure for polystyrene produces random substitution of the polymer142.
SPS13.5 samples were prepared with ionic concentrations ranging from 0.20 to 2.7 mol%
(i.e., percent of styrene moieties that were sulfonated).

Fully neutralized alkali metal salts of SPS13.5 were prepared by adding a 50 mol%
excess of an appropriate metal hydroxide or acetate to a 15 wt% solution of SPS in a 90/10
(v/v) mixture of toluene and methanol. After mixing the solution at room temperature for
30 min, the neutralized SPS salt was recovered by precipitating in boiling deionized water,
washed, and dried using the same procedures as described above for the SPS. The sample
nomenclature used herein is MSPS-\(p\), where M denotes the metal cation (Na\(^+\), K\(^+\), Rb\(^+\),
Cs\(^+\)) and \(p\) represents the ionic content in mol%.

All the ionomer blends used in this study were prepared from the MSPS-2.7 and
NSPS-0.20 ionomers by co-dissolution of the two in a mixed solvent of 90/10 (v/v) toluene
and methanol. The blend samples were isolated from solution using the same procedures
described above for isolating the neat ionomers. The sample nomenclature for the blend
samples is M\(x\)N\(y\), where M and N are the metal cations of MSPS-2.7 and NSPS-0.20
ionomers and \(x\) and \(y\) are the weight percentage of MSPS-2.7 and NSPS-0.20 ionomer. For
example, Na60Cs40 denotes a blend of 60 wt% NaSPS-2.7 and 40 wt% CsSPS-0.20. The
neat ionomers, MSPS-2.7 and NSPS-0.20, are denoted as M100N0 and M0N100, respectively – e.g., Na100Na0 and Na0Na100 represent the NaSPS-2.7 and NaSPS-0.20 ionomers.

4.2.2 Materials characterization

Dynamic oscillatory shear experiments were carried out with a TA Instruments ARES-G2 rheometer. Dynamic isothermal frequency sweeps were performed over a temperature range of 100 - 250ºC and a frequency range of 0.16 - 250 rad/s using either 25 or 8 mm parallel plates. All dynamic measurements were made within the linear viscoelastic (LVE) regime, which was determined from strain sweep experiments. TTS master curves were constructed using the same reference temperature, $T_r = 140$ºC, for all of the blends and the same shift factors for both $G'$ and $G''$ that were calculated by the TA Instruments’ TRIOS software. The glass transition temperatures for the ionomers varied by less than 10ºC, so the error introduced by using the same $T_r$ for comparing the LVE of the ionomers was expected to be small.

4.3 Results and discussion

This section discussed the effect of sulfonation degree and metal cation on the rheological behavior of neat ionomers and ionomer blends, and then compared the experimental data with model predictions.

4.3.1 Neat ionomers

The gel point for an associating polymer, where each chain on average has one sulfonate group\textsuperscript{155}, occurs at a sulfonate concentration (mol %) defined by Eq. 4.1,
\[ p_c = \frac{1}{N-1} \times 100 \text{ mol}\% \]  

where \( N \) is the degree of polymerization\(^{154} \). Eq. 4.1 assumes that each sulfonate group interacts with another sulfonate group to provide a physical crosslink. For the SPS\(_{13.5} \) ionomers, \( p_c = 0.78 \) mol\%. Below the gel point \( (p < p_c) \), the polymer system is a sol without the formation of percolated network. At the gel point \( (p = p_c) \), a percolated network (gel) exists, but the fraction of gel in the sample is very small. Above the gel point \( (p > p_c) \), the sol and gel are in equilibrium and the fraction of gel increases with \( p \), until the system is completely gelled at \( p = 2p_c \).\(^{154} \)

\( G' \) and \( G'' \) master curves at \( T_r = 140^\circ C \) for SPS-0.20 \( (p < p_c) \) and SPS-2.7 \( (p > 2p_c) \) ionomers with different alkali metal cations are shown in Figure 4.1. For SPS-0.20 neutralized with Na, K, Rb and Cs, no plateau was observed in \( G' \) (Figure 4.1a) and TTS worked well for each ionomer. Increasing the Coulomb energy of the ion-pair \( (E_c \sim 1/a, \text{ where } a \text{ is the ionic radius of the sulfonate cation}) \) did not significantly change the shape of \( G' \) and \( G'' \), but it increased their values slightly, especially at low frequency. The changes of \( G' \) and the melt viscosity \( (G''/\omega) \) by varying the Coulomb energy of the cation were smaller than those reported in previous studies of SPS ionomers\(^{32, 66, 80, 85, 154} \). That is because the sulfonate concentrations used in the previous studies of SPS ionomers were near or above the gel point, where the ionic dissociation time becomes a significant factor in determining the terminal relaxation. For the SPS-0.20 ionomers \( (p < p_c) \), the sulfonation level was far below the gel point where the terminal relaxation is determined mainly by the
Rouse relaxation time of the clusters without dissociation. Although the reversible gelation model does not account for the small effect of Coulomb energy on the terminal region of $G'$ for $p < p_c$, the model reasonably predicted the LVE behavior of all the SPS-0.20 samples.

![Figure 4.1 Master curves of $G'$ (filled symbols) and $G''$ (open symbols) with $T_r = 140^\circ C$ for (a) MSPS-0.20, and (b) MSPS-2.7 ionomers. Solid curves are model predictions.](image)

For $p > p_c$, Figure 4.1b, TTS failed in $G''$ for all four alkali metal salts of SPS-2.7 due to the different $T$ dependences of the ionic dissociation and the Rouse relaxation times$^{32, 80, 85, 154}$. $G_N$ was independent of the cation which agrees with the model prediction for $p > \ldots$

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though the model over-predicted the value of $G_N$ as discussed above. Increasing $E_c$
shifted the terminal relaxation to lower frequency by more than 2 orders of magnitude,
which was not unexpected, since the terminal relaxation is governed mainly by ionic
dissociation.

Table 4.1 summarizes the values of the Rouse relaxation time of an Kuhn segment ($\tau_0$)
and the ionic dissociation time ($\tau_s$) used in the model predictions in Figure 4.1 (solid
curves). Note that both $\tau_s$ and $\tau_0$ were determined from the nonlinear least square fit of
dynamic moduli. Decreasing $E_c$ (i.e., increasing the cation radius) had only small effect on
$\tau_0$ for the SPS-0.20 and SPS-2.7 ionomers, but it reduces $\tau_s$ by two orders of magnitude as
the cation was changed from Na to Cs.

Table 4.1 Rouse relaxation time ($\tau_0$) and ionic dissociation time ($\tau_s$) used for SPS-0.20
and SPS-2.7 ionomers at 140°C.

<table>
<thead>
<tr>
<th></th>
<th>SPS-0.20</th>
<th>SPS-2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>K</td>
</tr>
<tr>
<td>$\tau_0$ (μs)</td>
<td>34</td>
<td>30</td>
</tr>
<tr>
<td>$\tau_s$ (s)</td>
<td></td>
<td>4650</td>
</tr>
</tbody>
</table>

As discussed in Chapter III, the segment relaxation time $\tau_0$ depends mainly on the
sulfonation degree $p$, while the ionic dissociation time $\tau_s$ is more sensitive to the Coulomb
energy of the ion pair. $\tau_0$ exhibited an exponential dependence on $p$, Eq. 4.2, see Figure 3.9,

$$\log \tau_0 \text{ (µs)} = 1.3 + 0.49p$$

(4.2)

which was used to estimate $\tau_0$ for the ionomer blends using $p = \bar{p}$, where $\bar{p}$ is the average sulfonation degree of the ionomer blends. The values $\tau_s$ obtained for the SPS13.5 ionomers with the same cation, but different $p$, were averaged and the averaged value, Table 4.2, was used for estimating $\tau_s$ of the ionomer blends.

Table 4.2 The average ionic dissociation time $\tau_s$ for the different cations at 140°C.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_s$ (s)</td>
<td>4050</td>
<td>380</td>
<td>93</td>
<td>21</td>
</tr>
</tbody>
</table>

The temperature dependence of the shift factors, $a(T)$, used to construct the master curves in Figure 4.1 was fit to the Williams-Landel-Ferry (WLF) equation (Table 4.3 and Figure 4.2). For each sulfonation level $a(T)$ was relatively independent of the cation, but the shift factors for SPS-0.20 had a weaker temperature dependence than those for SPS-2.7. For the SPS-0.20 ionomers, the WLF constants were $C_1 = 7.3 \pm 0.2$ and $C_2 = 102 \pm 3.0$ K, and for SPS-2.7, $C_1 = 11.4 \pm 0.2$ and $C_2 = 129 \pm 2.2$ K. The shift factors for the ionomer with the lower sulfonate concentration are consistent with the fit of the parent PS, which is consistent with the fact that the Rouse motions of the polystyrene backbone dominate the LVE behavior when $p < p_c$. However, for $p > 2p_c$ the ionic-dissociation time becomes
important\textsuperscript{76} and influences the WLF fit. The free volume theory upon which the WLF equation is derived predicts that $C_1 \propto 1/f_r$ and $C_2 \propto f_r/\alpha_f$, where $f_r$ is the fractional free volume at $T_r$ and $\alpha_f$ is the free volume expansion coefficient\textsuperscript{71}. Thus, the changes in the WLF constants for the two ionomers indicate that the fractional free volume and the volume expansion coefficient decreased by $\sim 35\%$ and $\sim 50\%$, respectively, as the sulfonation level was increased from 0.20 to 2.7 mol%. That result is in qualitative agreement with the densification of SPS and PSMA ionomers due to the strong associative interactions that arise from the strong ionic or dipole-dipole interactions\textsuperscript{66,73}.

Figure 4.2 Temperature dependence of the experimental shift factors ($a_T$) for SPS-0.20 and SPS-2.7 ionomers, where the reference temperature, $T_r$, was 140\textdegree C. The black and red solid lines are the least-square fit of WLF equation for SPS-0.20 and SPS-2.7 ionomers, respectively.
Table 4.3 WLF Constants for PS13.5, SPS-0.20, and SPS-2.7 ionomers.

<table>
<thead>
<tr>
<th></th>
<th>SPS-0.20</th>
<th></th>
<th>SPS-2.7</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PS13.5</td>
<td>Na K Rb Cs</td>
<td>Na K Rb Cs</td>
</tr>
<tr>
<td>C₁</td>
<td>7.5</td>
<td>7.3</td>
<td>7.5</td>
</tr>
<tr>
<td>C₂ (K)</td>
<td>106.5</td>
<td>99.9</td>
<td>105.4</td>
</tr>
</tbody>
</table>

4.3.2 Binary ionomer blends

The LVE behavior of ionomer blends was studied using binary mixtures of SPS-0.20 and SPS-2.7 ionomers, where the former component had a sulfonation level far below the gel point, \( p \ll p_c \), and the latter ionomer had a sulfonation level far above the gel point, \( p > 2p_c \). The properties of blends where the two ionomers had the same counterion (Na) were first evaluated to compare their LVE behavior to a neat ionomer with a comparable total sulfonate concentration, and then mixtures of ionomers with different counterions were studied to determine how the properties were influenced by the two separate cations. The average ionic content (\( \bar{p} \)) of the mixture MₓNᵧ was calculated from a mass average,

\[
\bar{p} = \frac{p_M x}{100} + p_N (1 - x/100)
\]  \( (4.3) \)

where \( x \) is the concentration of SPS-2.7 (wt%) and \( p_M \) and \( p_N \) are the ionic contents (mol%) of the SPS-2.7 and SPS-0.20, respectively. The gel point for the neat ionomers, \( p_c = 0.78 \text{ mol\%} \), was also used for the blends, since the molecular weights of the two components of the mixture were the same. It is important to note that for the SPS ionomer
blends it does not appear that cation-exchange between the two components of the blend occurs in the melt, at least during the time of the experiments described herein. The evidence for that conclusion will be discussed later in this paper, but that conclusion marks an important distinction between PEMA ionomer blends, where cation exchange in the melt has been reported, facilitated by the unneutralized carboxylic acid groups.\textsuperscript{158}

**Blends of ionomers with the same counterion.** Master curves of ionomer blends $Na_xNa_y$ are shown in Figure 4.3. The $p$-dependence of the LVE behavior is similar to that observed for the neat ionomer melts that was discussed earlier in Chapter III. When the blend contained 10 wt% of NaSPS-2.7 ionomer ($Na_{10}Na_{90}$), both $G'$ and $G''$ exhibited power law behavior, $G'(\omega) \sim G''(\omega) \sim \omega^\theta$, in the intermediate frequency range, which is consistent with the model prediction for $p < p_{\theta 1}$.\textsuperscript{154} When the concentration of NaSPS-2.7 increased to 20 wt% ($Na_{20}Na_{80}$), $\bar{p} \sim p_c$, similar to the LVE behavior of the neat ionomers, the blend exhibited a clear transition from mean field behavior, $G'(\omega) \sim G''(\omega) \sim \omega^\theta$, to critical percolation behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{2/3}$. The appearance of the critical percolation region indicates that the composition of the ionomer blend was close to the gel point, which validates the assumption that the same gel point is applicable for the neat ionomer and the binary blends corresponding always to an average of one sulfonate group per chain. When $\bar{p} > p_c$ ($Na_{30}Na_{70}$), a weak plateau in $G'$ was observed, Figure 4.3a, which became more distinct as $\bar{p}$ increased, i.e., increasing MSPS-2.7 concentration. $G_N$ for the blend also increased with increasing $\bar{p}$, which is consistent with increasing the effective crosslink density.
Figure 4.4 compares the LVE behavior of two blends with that of two neat ionomers with similar sulfonation level: 1) Na20Na80 (\( \bar{p} = 0.70 \) mol\%) and NaSPS-0.76 (\( p = 0.76 \) mol\%) and 2) Na40Na60 (\( \bar{p} = 1.2 \) mol\%) and NaSPS-1.2 (\( p = 1.2 \) mol\%). The compositions of the first pair are close to the gel point and for the second pair \( p_c < p < 2p_c \).

For the \( p \sim p_c \), the LVE behavior of the neat ionomer and the ionomer blend were similar, though there was a small difference in the values of \( G' \) and \( G'' \) at intermediate frequencies. For \( p > p_c \) the qualitative trends of the LVE behavior were similar, but \( G_N \) for the blend was distinctly lower than for the neat ionomer and the data in the peak region of \( G'' \) differed considerably. These differences are attributed to differences in the sulfonate distribution in the blends and the neat ionomers, as is discussed below.
Figure 4.3 Master curves of $G'$ (filled symbols) and $G''$ (open symbols) for NaSPS-0.20 (Na0Na100), NaSPS-2.7 (Na100Na0) and blends of NaSPS-0.20 and NaSPS-2.7 ionomers (Na$_x$Na$_{1-x}$). $T_r = 140^\circ$C. The numbers in the parentheses of the legend are $\overline{p}$ and the solid curves are the model predictions. The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior and (III) terminal behavior.
Figure 4.4 Comparison of LVE behavior for binary blends and neat ionomers with similar ionic contents at 140°C. The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior and (III) terminal behavior.

In general, for the neat ionomers and blends TTS worked well when $p < p_c$, but for $p \sim p_c$ superposition of $G'$ failed in the terminal region and for $p > p_c$ $G''$ failed in the intermediate frequencies prior to the terminal region. When $p > p_c$, the failure of TTS for $G''$ was more apparent at the frequencies above the peak in $G''$, but the $G'$ data appeared to obey TTS. The success of TTS for $G'$, but not $G''$ is comparable to the results of Shahamy and Eisenberg\textsuperscript{78} and Earnest and MacKnight\textsuperscript{79} for carboxylate ionomer melts, where they also found that TTS worked for their $G'$ data, but not for the $G''$ data. TTS failed only when the viscous dissipation associated with the ionic aggregates became important. Earnest and MacKnight\textsuperscript{79} attributed this behavior to changes in the shift factors for short and long relaxation times, which were associated with two relaxation process with different temperature dependences\textsuperscript{71}.

Figure 4.5 shows the temperature dependence of the shift factors for the master curves.
in Figure 4.3. For $x \leq 30$ wt% ($\bar{\rho} \leq 0.95$), the shift factors for the PS13.5 and the Na$_x$Na$_y$ blends were fitted with the WLF equation with $C_1 = 7.3 \pm 0.2$ and $C_2 = 99.7$ K $\pm 3.7$ K, Table 4.4, which were similar to the values used for the neat ionomers for $p < p_c$ as was discussed earlier. For $x \geq 30$ wt%, the constants needed to fit the WLF equation began to deviate from those values, Table 4.4. In general, $C_1$ and $C_2$ increased with increasing $p$. The changes in the constants corresponded to decreases of the fractional free volume by $\sim 30\%$ and the volume expansion coefficient by $\sim 50\%$ when the blend composition changed from $\bar{\rho} < p_c$ to $\bar{\rho} \gg 2p_c$. Those changes are similar to the densification and change in the volume coefficient of expansion of the neat ionomers discussed earlier in this paper, and they are consistent with the explanation that for $p > p_c$, the relaxation associated with the ionic dissociation time of the ionic or dipolar interactions dominate the viscoelastic behavior of the melt.

Table 4.4 WLF Constants for Na$_x$Na$_y$ ionomers.

<table>
<thead>
<tr>
<th></th>
<th>PS13.5</th>
<th>Na$_x$Na$_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x = 0$</td>
<td>$x = 10$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>7.5</td>
<td>7.3</td>
</tr>
<tr>
<td>$C_2$(K)</td>
<td>106</td>
<td>99.9</td>
</tr>
</tbody>
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Figure 4.5 Time-temperature shift factor $a_T$ for NaSPS-0.20 (Na0Na100), NaSPS-2.7 (Na100Na0), and blends of NaSPS-0.20 and NaSPS-2.7 ionomers (Na$x$Na$y$) with $T_r = 140^\circ$C. The solid lines show the WLF fits.

Figure 4.4 indicates that when $p > p_c$, a binary blend of two ionomers has a broader distribution of relaxation times than a neat ionomer with the same value of $p$. This difference may be related to the distribution of ionic groups per chain. Because the sulfonation reaction is random\textsuperscript{142}, each polymer chain may contain different numbers of sulfonate groups. Some chains have more than, and some chains less than, the average sulfonation level. The distribution of ionic groups per chain can be represented by a binomial distribution\textsuperscript{142},

$$P(x) = \frac{N!}{x!(N-x)!} p^x (1-p)^{(N-x)}$$  \hspace{1cm} (4.4)

where $P(x)$ is the probability that for an ionomer with ionic concentration $p$, a chain
with a degree of polymerization $N$ will have $x$ ionic groups.

Figure 4.6 compares the distribution of ionic groups per chain, $P(x)$, for two binary blends of NaSPS-0.20 and NaSPS-2.7 and the neat ionomer with a similar sulfonation level. The calculations assumed a constant value of $N = 130$ for each chain (note that the polydispersity index was 1.06). The distribution of ionic groups per chain is different for the binary blend and neat ionomer with similar $p$, but both materials had similar concentrations of chains with $x = 0$ and $x = 1$, which do not contribute to the gel network. That may be why the dynamic modulus for the blends and neat ionomer overlapped at the lower melt temperatures where short time relaxation processes should dominate. It also explains the lower $G_N$ predicted by the reversible gelation model, since the chains with $x \leq 1$ cannot form stress-bearing strands of the network. However, the sulfonate distributions of the blends were skewed to higher values of $P(x)$ for $x \geq 2$. For example, although Na20Na80 blend had fewer functional chains (i.e., $P(x \geq 2)$) than NaSPS-0.76, the functional chains with $x \geq 2$ in the blend had higher average functionality ($\bar{x} \approx 3.7$) than NaSPS-0.76 ($\bar{x} \approx 2.4$). A comparison of Na40Na60 and NaSPS-1.2 produced similar results. The effect of the sulfonation distribution being skewed towards higher sulfonation levels should be similar to that of a higher molecular weight tail of the molecular weight distribution for an entangled polymer, but the effect of increasing ionic groups per chain on the viscosity and elasticity of an ionomer melt is much stronger than the effect of increasing chain entanglements$^{32}$. As a result, the higher ‘$x$’ end of the sulfonate distribution shown in Figure 4.6 has a disproportionate influence on the relaxation time.
distribution and produces longer relaxation times for the blends than for the neat ionomers with similar sulfonation levels.

Figure 4.6 Distribution of sulfonate groups per chain calculated from Eq. 4.4 for the binary blends and neat ionomers used for Figure 4.4.

The model predictions of the experimental data for the Na$_x$Na$_y$ blends shown in Figure 4.3, capture the qualitative trend for the changes in $G'$ and $G''$. Although the model fit well for the $G''$ data for $\bar{p} < p_c$ (Na10Na90), an obvious discrepancy between the model predictions and the experimental data is clearly seen in the terminal region of $G'$. With the exception of the ionomer with the lowest sulfonation level, NaSPS-0.066, a similar disagreement between the theory and experiment was observed for the neat ionomers with $p < p_c$, see Figure 3.4 and 4.1. As was discussed earlier in Chapter III for the neat ionomer data, the lack of fit of the model may be due to the failure to account for the non-effective breakup of the clusters. The reversible gelation model and the experimental data for the
Blends agreed when $\bar{p} \sim p_c$ (Na20Na80), but for $\bar{p} > p_c$ the model over-predicted $G''$ in the terminal region. Although the model predicted a plateau region in $G'$, it over-predicted $G_N$ and predicted a sharper onset of terminal response than observed. The higher $G_N$ prediction is due to the assumption that all the strands between ionic groups are stress bearing. However, strands with two ionic groups that join the same clusters form loops and chains with only one or no ion-pairs form dangling chains that do not contribute to $G_N$. The onset of terminal behavior for the blends was more gradual than for the neat ionomers, c.f., Figures 3.4 and 4.4. That difference and the failure of the model to predict the slower relaxation response are also likely due to the differences in the sulfonate distribution shown in Figure 4.6 and the failure of the model to account for difference in the sulfonate distribution.

**Blends of ionomers with different counterions.** The effect of using different cations for the two ionomer components on the LVE behavior of a blend was studied using three blend compositions: M10N90 ($\bar{p} < p_c$), M20N80 ($\bar{p} \sim p_c$) and M60N40 ($\bar{p} > 2p_c$). For each blend composition, the cation of one ionomer component was varied (Na, K, Rb and Cs), while the cation of the other ionomer component was fixed. It did not appear that any significant cation-exchange occurred in these ionomers. That possibility was assessed by mixing ionomers with two different sulfonation levels and cations. As will be shown and discussed below, the viscosity of a blend of a high and low sulfonation level with different cations is dominated by the cation on the ionomer with the higher sulfonation level. Thus, if cation-exchange occurred, one would expect that the elasticity and viscosity of the melt
would change appreciably with time. To assess that possibility, the storage modulus ($G'$) and the dynamic viscosity ($G''/\omega$) at 180°C of a 20/80 (w/w) blend of CsSPS-2.7 and NaSPS-0.20 were monitored during cyclic frequency sweeps for 7 h, and no significant changes in either occurred.

One focus in this study was the effect of the mixing of ions. In order to quantify its effect, a hypothesis was proposed that the dissociation rate, i.e., the frequency of dissociation, of a given type of ions in a blend was independent of the presence of the other type of ion. Thus, the average frequency of ionic dissociation was assumed to be a weighted average of the frequencies for the different cations,

$$\bar{\omega} = \phi_1 \omega_{s1} + \phi_2 \omega_{s2}$$

where $\phi_i$ is the mole fraction of each cation in the blend (i.e., the mole fraction of cation $i$ of the total number of sulfonate groups in the blend) and $\omega_{si}$ is its frequency of dissociation for cation $i$. The average ionic dissociation time for the blend is then,

$$\frac{1}{\tau_{sb}} = \frac{\phi_1}{\tau_{s1}} + \frac{\phi_2}{\tau_{s2}}$$

where $\tau_{si}$ is the ionic dissociation time for each cation obtained from the neat ionomers, Table 4.2.

Figure 4.7 shows the master curves for M10N90 blends. In Figure 4.7a the cation for the NSPS-0.20 component was fixed as Na (M10Na90 blends) and in Figure 4.7b the cation for the MSPS-2.7 component was fixed as Na (Na10N90 blends). For high and
intermediate frequencies the $G'$ and $G''$ data for the four M10Na90 blends superposed and exhibited mean-field behavior, $G'(\omega) \sim G''(\omega) \sim \omega^1$, which qualitatively agrees with the model prediction for $\bar{p} < p_c$. However, the model over-predicted the two moduli for the intermediate frequencies and under-predicted $G'$ for the lowest frequencies. In the terminal region, the $G''$ data for the four M10Na90 blends superposed, but $G'$ for the four blends were different, decreasing with the decrease of Coulomb energy, $E_c$. Similar with the predictions for the SPS-0.20 ionomers, c.f. Figure 4.1, the reversible gelation model failed to account for the effect of $E_c$, because it assumes that $\tau_s$ has a negligible effect on the terminal relaxation when $\bar{p} < p_c$, at which the relaxation time of the largest cluster is still shorter than $\bar{\tau}_{ib}$.

Figure 4.7 Master curves of $G'$ (filled symbols) and $G''$ (open symbols) with $T_r = 140^\circ$C for (a) M10Na90 and (b) Na10N90 blends where $\bar{p} = 0.45$ mol\% $< p_c$. The solid curves are the model predictions. The colored regions correspond to: (I) mean field percolation behavior, and (II) terminal behavior.
Figure 4.8 Master curves of $G'$ (filled symbols) and $G''$ (open symbols) with $T_r = 140^\circ$C for (a) M20Na80 and (b) Na20N80 with $\bar{p} = 0.7 \text{ mol}\% \sim p_c$. The solid curves are the model predictions. The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior and (III) terminal behavior.

As with the neat ionomer with $p \sim p_c$, the LVE behavior of the M20Na80, Figure 4.8 (a), and Na20N80, Figure 4.8b, blends exhibited three distinct power law relaxation regions:

1) mean field behavior, $G'(\omega) \sim G''(\omega) \sim \omega^1$ ;
2) critical percolation behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{2/3}$ ; and
3) terminal behavior, $G'(\omega) \sim \omega^3, G''(\omega) \sim \omega^1$. TTS failed for $G'$ in the terminal region for both blend compositions and each set of cations used, due to the overlap of the of the ionic dissociation and Rouse relaxation processes. Decreasing $E_c$ increased the frequency of the onset of terminal behavior as a consequence of decreasing...
$\tau_s$. Whereas, the divergence of only the $G'$ data for the different cations was observed, for $\bar{p} < p_c$ in Figure 4.7, for $\bar{p} \sim p_c$ in Figure 4.8, both $G'$ and $G''$ decreased with decreasing $E_c$ in the terminal region, with larger changes occurring in $G'$.

When $\bar{p} > p_c$, see the LVE behavior of the M60Na40 blends in Figure 4.9, $G'$ exhibited a distinct plateau and TTS failed in the valley of $G''$ before the terminal relaxation because of the overlap of two relaxation processes with different temperature dependences, the terminal relaxation that is governed by the ionic dissociation time ($\tau_i$) and the Rouse relaxation time ($\tau_X$) at higher frequency before the valley. The choice of the cation did not affect $G_N$, which agrees with the results for the neat SPS-2.7 ionomers, Figure 4.1, and other LVE data for similar SPS ionomers with $p > 2p_c^{32,80}$. The reversible gelation model correctly predicts that the $G_N$ is independent of cation when the gel was formed at $p > p_c^{154}$. For the M60Na40 blends, Figure 4.9a, the terminal relaxation time increased by two orders of magnitude by increasing $E_c$ of cation M by 56%, i.e., changing it from Cs to Na. However, for Na60N40 blends, where the cation M of SPS-2.7 was fixed as Na, increasing $E_c$ of cation N by 56% (changing N = Cs to N = Na) only increased the terminal relaxation time by one order of magnitude, Figure 4.9b. When M was fixed as Cs, i.e., Cs60N40 blends, Figure 4.9d, the same increase of $E_c$ had little effect to the terminal relaxation time. These results indicate that for $\bar{p} > p_c$, the terminal behavior is dominated by the choice of the cation (M) on the SPS-2.7 ionomer, since the SPS-2.7 contributes to 95% of the total cation. Thus, the LVE behavior of an ionomer blend can be tuned considerably by varying the cation on the component with higher sulfonation ($p$).
Figure 4.9 Master curves of $G'$ (filled symbols) and $G''$ (open symbols) with $T_r = 140 \, ^\circ C$ for (a) M60Na40, (b) Na60N40, (c) K60N40, (d) Cs60N40 samples with $\bar{p} = 1.7$ mol\% > 2$p_c$. The solid curves are the model predictions.

With the use of Eq. 4.6 to calculate $\bar{\tau}_{sb}$ the reversible gelation model predicted the LVE behavior of the M60N40 blends reasonably well, except for an overestimation of $G_N$, Figure 4.8, which as discussed earlier is believed to be due to the assumption of an ideal supramolecular network. Even with the discrepancies between the reversible gelation model prediction and the experimental data shown in Figures 4.7 and 4.8, the model provided a remarkably good prediction of the changes of the terminal relaxation times as $E_c$ was varied for all the M60N40 blends ($\bar{p} > p_c$), where the network was well-developed.
and the terminal relaxation was governed by the ionic dissociation time.

The validity of the mixing rule proposed by Eq. 4.6 was further confirmed in Figure 4.10, which plots $\bar{\tau}_{sb}$ against the ionic dissociation time of the blend, $\tau_s'$, calculated from terminal relaxation time, $\tau$, which is determined directly from the experimental data in the terminal region,

$$\tau_s' = \left(\tau / \tau_X^{1/4}\right)^{4/3} \quad \text{for } p_{e1} < \overline{p} < p_{e2}$$  \hspace{2cm} (4.7)

$$\tau_s' = \tau / \varepsilon \quad \text{for } p_{e2} \leq \overline{p} < 2p_c$$  \hspace{2cm} (4.8)

$$\tau_s' = \tau / \varepsilon^2 \quad \text{for } \overline{p} \geq 2p_c$$  \hspace{2cm} (4.9)

where $\tau_X$ is the Rouse relaxation time of the precursor (PS) chain and $\varepsilon$ is the relative extent of gelation, which is a measure of how far the system is from the gel point.\(^{154}\)

$$\varepsilon = (p - p_c) / p_c$$  \hspace{2cm} (4.10)

$\tau$ was calculated from Eq. 4.11.\(^{71}\)

$$\tau = \lim_{\omega \to 0} \left[ \frac{G'(\omega)}{\omega G''(\omega)} \right]$$  \hspace{2cm} (4.11)

The linear relationship between $\bar{\tau}_{sb}$ and $\tau_s'$, $\bar{\tau}_{sb} \propto (\tau_s')^1$, confirms the mixing rule proposed in Eq. 4.6, which now provides a convenient method for predicting the terminal properties of at least these SPS ionomer blends.
Figure 4.10 Test of the validity of the linear additivity of breakup frequency for the ionomer blends. \( \bar{\tau}_{sb} \) was calculated from the mixing rule, Eq. 4.6, \( \tau'_s \) was calculated from the measured terminal relaxation time \( \tau \) using Eqs. 4.7-4.9. The black solid line is the linear fit, and the dashed lines are the 95% confidence limit of the linear fit. The legend denotes the cation pairs as M-N for M\textsubscript{x}N\textsubscript{y} blends.

4.4 Conclusions

The reversible gelation model for the LVE properties of ionomers proposed in Chapter III was further tested for a higher molecular weight SPS ionomer and including materials with \( p < p_c \) and blends of two ionomers with different sulfonation levels and cations. Although the reversible gelation model with only two parameters, the Rouse relaxation time and an ionic dissociation time, predicted the LVE properties of ionomer melts reasonably above the gel point (\( p > p_c \)), it failed to accurately predict \( G' \) in the terminal region for ionomers with \( p < p_c \), though it predicted \( G'' \).
Binary blends of SPS ionomers exhibit a sol-gel transition at the identical gel point, $p_c$, as a neat ionomer if one uses a simple mass averaged mixing rule to calculate an average sulfonation level for the blend. However, even for the same average ionic group concentration, binary SPS ionomer blends show different LVE behavior than a neat ionomer. That is because the random nature of the sulfonation reaction produces different ion-pair distributions for ionomer samples with different values of $p$, and mixing two ionomers with different values of $p$ produces a broader distribution of relaxation times than either of the neat ionomer components. The broader relaxation distribution of relaxation times produces a longer terminal relaxation time. It also produced a lower value of the plateau modulus, $G_N$, as a consequence of broadening the ion-pair distribution on the chains that may create more chains with one or no sulfonate groups that relax more rapidly and/or differences in the non-equilibrium distribution of ionic associations that arise from decreases in molecular mobility as the material gels.

A linear mixing rule for the dissociation frequency of the ionic or dipolar interactions in was proposed for binary blends, and it worked well for blends of two SPS ionomers with different sulfonation levels and different cations. The mixing rule can be easily extended for mixtures of greater than two components,

$$\frac{1}{\tau_{sb}} = \sum \phi_i \frac{1}{\tau_{si}}$$

(4.12)

When the mixing rule is incorporated, the reversible gelation model qualitatively
predicts the LVE behavior of ionomer blends with various compositions and cations. Although the model fails to quantitatively predict the terminal response of blends with $\bar{p} < p_c$, for the identical reasons for why it does not work for neat ionomers, the model provides a good prediction for the terminal relaxation time of ionomer blends with $\bar{p} > 2p_c$, where the ionic dissociation frequency controls LVE behavior. Thus, the incorporation of the mixing rule proposed herein for the ionic dissociation time, $\tau_{sd}$, for ionomer blends provides a convenient method for predicting a priori the terminal relaxation time of a blend and, at least, qualitatively predicting its LVE behavior. The incorporation of the effects of the distribution of ionized sites into the percolation model remains a problem that needs to be addressed if the model is to provide more quantitative predictions of the LVE behavior of neat ionomers and blends.
CHAPTER V

NONLINEAR RHEOLOGY OF RANDOM SULFONATED POLYSTYRENE IONOMERS: THE ROLE OF THE SOL-GEL TRANSITION*

5.1 Introduction

Ionomers are relatively hydrophobic polymers with small amounts of covalently attached ionic groups (typically, less than 15 mol%), such as sulfonic and carboxylic acids neutralized with metal or ammonium counterions. Ionomers have wide applications as membranes,146 compatibilizers for polymer blends,147 shape memory polymers and self-healing materials.145 The applications take advantage of the ionic interactions that occur in these materials, which modify their microstructure and the physical, mechanical, and rheological properties. In bulk ionomers, the polar ionic groups usually associate with each other due to the strong electrostatic or dipolar attractions in a relatively non-polar polar polymer medium. Inter-chain associations take the role of physical crosslinks that persist for long times and/or to high temperature.159

The nonlinear rheology of SPS and other bulk ionomers has been previously studied,2, 32, 58, 63, 68, 69, 85, 127 but in all the prior studies the concentration (mole fraction) of the ionic

* The work discussed in this chapter was submitted to Macromolecules.
species, \( p \), was much higher than the gel point \( p_c \), where \( p_c = \frac{1}{(N-1)} \times 100 \text{ mol}\% \) for a bulk ionomer with a degree of polymerization \( N \).\textsuperscript{154} At the gel point, each SPS chain contains on average one sulfonate group. For unentangled ionomers, one characteristic of their linear viscoelastic (LVE) properties when \( p > p_c \) is the appearance of a rubber-like plateau in \( G'(\omega) \) at frequencies below the rubber to glass transition. For high molecular weight, entangled polymers, \( p_c \) is very low and it is difficult to prepare samples with \( p < p_c \). For example, Yu and Weiss\textsuperscript{67} reported the rheological behavior of SPS ionomers (\( M = 400,000 \text{ g/mole} \)) with a sulfonation level of \( p = 0.10 \), but even for that low sulfonation, \( p > p_c \) (= 0.026).

Recently, randomly sulfonated oligomeric polystyrene (SPS) ionomers have been used as a model system for studying the dynamics of ionic associations and the relaxation behavior due to dissociations and \textit{ion-pair hopping}.\textsuperscript{32, 80, 85, 154, 155, 160} There are two major advantages of using low molecular weight ionomers: one is that the properties are influenced only by the effects of ionic interactions owing to the absence of chain entanglements and the other advantage is that it allows one to study ionomers below and near the gel point \( p_c \).

The mean-field theory, developed previously for the dynamics of associative polymer solutions by Rubinstein and Semenov,\textsuperscript{136, 137} was recently modified for bulk ionomers.\textsuperscript{154} The reversible gelation model\textsuperscript{13} predicts two transitions in the relaxation behavior when \( p \) approaches \( p_c \) from the sol state. One transition occurs at the Ginzburg point\textsuperscript{156}, above which the newly formed branched chains, termed \textit{clusters} (note that the term \textit{clusters} used
herein is different from the term commonly used to describe ionic nanodomains in other ionomer literature), are at their overlap concentration, and the growth of branched chain are accordingly governed by critical percolation instead of mean-field percolation. The other transition occurs close to the gel point, where the Rouse relaxation time of the clusters becomes longer than the effective breakup time, above which the terminal relaxation is controlled by effective breakup, when breakup of the cluster occurs on the chain backbone and produces two daughter clusters of comparable size with relaxation times much shorter than their mother cluster. In contrast, non-effective breakup occurs at the side-chain and produces one daughter cluster having similar size as the mother cluster and another smaller satellite cluster. The reversible gelation model with only two variables, the Rouse time of an Kuhn segment, $\tau_0$, and the ionic dissociation time, $\tau_s$, quantitatively predicts the LVE behavior of neat SPS ionomers and their binary blends, as well as the sol-gel transition.

The non-linear behavior of SPS ionomer melts with $p > p_c$ has been reported to exhibit strain-hardening, where the transient viscosity before yielding is higher than that predicted from LVE behavior, in extensional flow, but not in shear flow. Shear-thickening is often observed for a variety of associative polymer solutions, but with the exception of reference 32, it has not been reported for bulk ionomer melts.

A hypothesis of the present work is that strain-hardening and shear-thickening for ionomer melts only occurs when $p \sim p_c$, which would explain why those phenomena have not previously been observed for ionomers with $p >> p_c$. This hypothesis was tested by
examining the nonlinear shear rheology of the oligomeric SPS samples with \( p < p_c, p \sim p_c, \) and \( p > p_c. \) Strain-hardening and shear-thickening were experimentally observed only when the system was close to the gel point, and under several additional conditions including proper strength of ionic association and temperature.

5.2 Experimental section

This section described the synthesis of SPS ionomers and the characterization of the rheological behavior of SPS ionomers.

5.2.1 Materials

Two oligomeric polystyrenes (PS) with weight average molecular weights \( M_w = 4.6k \) and 13.5k g/mol, and narrow polydispersity (PDI < 1.06) were purchased from Pressure Chemical Co. (Pittsburgh, PA). The two PS samples are denoted as PS4.6 and PS13.5, respectively. Concentrated sulfuric acid, 1,2-dichloroethane (DCE), acetic anhydride, toluene, methanol were purchased from Sigma-Aldrich and used as received.

PS was sulfonated using acetyl sulfate as the sulfonating agent. Acetyl sulfate was prepared by adding concentrated sulfuric acid to a 60 mol% excess of acetic anhydride in DCE at 0°C, and the freshly prepared acetyl sulfate was then added over one minute to a continuously stirred 10 wt% PS/DCE solution (~200ml) at ~50°C. The reaction was terminated after 1 h by adding ~2 ml of 2-propanol. The SPS was isolated by precipitation in boiling di-ionized (DI) water, washed three times with DI water, dried in air at 70°C for 1 day and finally dried at 120°C in a vacuum oven for 1 week. The sulfonation level was determined by sulfur elemental analysis by Robertson Microlit Analysis (Madison, NJ).
The sulfonation reaction occurs randomly along the polymer chain, principally at the para-position of the phenyl ring\textsuperscript{157}, and produces a distribution of chains with varying sulfonation, including some with no sulfonate groups, that can be represented by a binomial distribution\textsuperscript{142}.

Alkali metal salts of SPS were prepared by adding a 1.5 equivalents of metal hydroxide or acetate to a 15 wt\% solution of the SPS acid derivative in a 90/10 (v/v) mixture of toluene and methanol. After 30 min, the neutralized SPS was isolated following the procedures described above for the sulfonic acid derivative. Six different samples were prepared with degrees of sulfonation $p$ of 1.6, 2.5, and 2.8 mol\% for SPS4.6 and 0.20, 0.76, and 1.2 mol\% for SPS13.5, which correspond to an average number of ionic groups per chain of 0.7, 1.1, and 1.2 for SPS4.6, and 0.3, 1, and 1.6 for SPS13.5. The sample nomenclature used hereafter is MSPS$_x$-$p$, where M denotes the cation (Na, K, Rb, Cs), $x$ is the molecular weight of the PS precursor (in kg/mol), and $p$ is the degree of sulfonation in mol\%.

5.2.2 Materials characterization

Linear and nonlinear rheological measurements were carried out with a TA Instruments ARES-G2 rheometer. Dynamic frequency sweeps were performed over a temperature range of $T = 90$ - 240\degree C and a frequency range of $\omega = 0.16$ - 250 rad/s using either 25 or 8 mm parallel plates. All dynamic measurements were made within the LVE region, which was determined from strain sweep experiments. Time-temperature-superposition (TTS) master curves were constructed at the same reference temperature $T_r$. 
= 140°C for comparison. For each molecular weight, the glass transition temperatures of the different ionomer samples varied by about 4°C, so the error in using the same $T_r$ for all samples was small. A cone and plate fixture with a diameter of 25 mm and a cone angle of 0.04 rad was used for steady shear and startup shear experiments. Those experiments were conducted over a temperature range of $T = 120 - 200°C$ and shear rates of $\dot{\gamma} = 0.0001 - 1000 \text{ s}^{-1}$.

5.3 Results and discussion

This section investigated the effect of sulfonation degree and metal cation on the linear and nonlinear rheological behavior of SPS ionomers, and then discussed the different steady shear and startup shear behavior.

5.3.1 Linear viscoelastic (LVE) behavior

Figure 5.1 shows the LVE master curves at $T_r = 140 °C$ for SPS4.6 and SPS13.5 ionomers with varying sulfonation levels and different cations. The gel points are $p_c = 2.3$ mol% and $p_c = 0.78$ mol% for the SPS4.6 and SPS13.5 ionomers, respectively. The Ginzburg point, the transition between mean-field and critical percolation, was defined as

$$p_g = \left(1 - N_K^{-1/3}\right) p_c$$

with $N_K$ as the number of Kuhn segments per chain. For SPS4.6 and SPS13.5 ionomer, the Ginzburg point corresponds to $p_g = 1.0$ and 0.47, respectively.

When the sulfonation degree is below the gel point, $p < p_c$, TTS works well for both NaSPS4.6-1.6 ($p_g < p < p_c$) and NaSPS13.5-0.20 ($p < p_g$) ionomers and no plateau was observed in $G'(\omega)$, see Figure 5.1a and 5.1b. The reversible gelation model predicts mean-
field behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{1}$, for $p < p_g$, which was not observed in NaSPS13.5-0.20 ionomer. For $p_g < p < p_c$, the NaSPS4.6-1.6 ionomer does not exhibit the predicted critical percolation behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{2/3}$, but, instead, it shows a power law of $G'(\omega) \sim G''(\omega) \sim \omega^{1}$ before the terminal region. The absence of the predicted power law relation in those ionomers may be attributed to the failure to incorporate the effects of non-effective breakup in the reversible gelation model.160

Figure 5.1 LVE master curves at $T_r = 140 \, ^\circ C$ for: (a) NaSPS4.6 and (b) NaSPS13.5 ionomers with varying sulfonation level; (c) SPS4.6-2.5 ($p \sim p_c$) and (d) SPS13.5-0.76 ($p \sim p_c$) ionomers neutralized with different cations. The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior and (III) terminal behavior. The solid curves are the model predictions.
When $p - p_c$, the SPS4.6-2.5 and SPS13.5-0.76 ionomers showed three distinct power law regions: 1) mean-field behavior, $G' \sim G'' \sim \omega^1$, at high frequencies, 2) critical percolation behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{2/3}$, at intermediate frequencies and 3) terminal relaxation, $G'(\omega) \sim \omega^2, G''(\omega) \sim \omega^1$, at low frequencies. For the SPS4.6-2.5 ionomers, $G'$ showed a very weak plateau before the terminal region, see the arrow in Figure 5.1c, probably due to their slightly higher $p$ than the predicted gel point ($p = 2.5$ mol$\% > p_c$). When $p$ is slightly above $p_c$, a small fraction of percolated network (gel) is formed in the ionomer, and the relaxation of the gel network contributes to the appearance of the weak plateau in $G'$. For the SPS4.6-2.5 and SPS13.5-0.76 ionomers, decreasing the Coulomb energy of the ion-pair, $E_c \sim 1/a$ where $a$ is the ionic radius of the cation (i.e., varying the cation from Na to Cs decreased $E_c$ by the ratios 1: 0.76: 0.70: 0.64), shifted the terminal relaxation to higher frequency as a consequence of decreasing the ionic dissociation time $\tau_s$.

TTS fails for both SPS4.6-2.5 and SPS13.5-0.76 ionomers due to the different temperature dependences of the Rouse relaxation of the precursor chain at high frequency and ionic dissociation in the terminal region. Specifically, the terminal relaxation of the SPS13.5-0.76 ionomer is governed by the effective breakup with the effective breakup time as $\tau_c \sim \tau_{X}^{1/4} \tau_{s}^{3/4}$, where $\tau_{X}$ is the Rouse relaxation of the precursor chain. Hence, TTS failed significantly in the terminal region of $G'$ since $\tau_c$ depends on $\tau_{X}$ and $\tau_s$. The effect is less for $G''$ because $G''$ is less sensitive to the slow relaxation modes than $G'$ (In general, the storage and loss modulus can be written as multiple Maxwell modes as $G'(\omega) = \sum p \omega^2 \tau_p^2/(1 + \omega^2 \tau_p^2)$
and \( G''(\omega) = \sum_p \omega \tau_p / (1 + \omega^2 \tau_p^2) \), \( G'(\omega) \) that scales with \( \tau_p^2 \) are more sensitive to slow modes with high \( \tau_p \) than \( G''(\omega) \) that scales with \( \tau_p \). For the same reason, \( G''(\omega) \) is more sensitive to fast modes than \( G'(\omega) \). TTS holds better in the terminal region for the SPS4.6-2.5 ionomer possibly because this sample is already slightly above the gel point where the terminal relaxation is governed by \( \tau_s \). Nevertheless, failure of TTS was observed before the terminal relaxation (indicated by arrow in Figure 5.1), where relaxation is dependent on Rouse motions and ionic dissociation.

When \( p > p_c \) (SPS4.6-2.8 and SPS13.5-1.2 ionomers), \( G' \) showed a well-defined plateau and \( G'' \) shows a peak before the terminal relaxation. TTS failed for SPS4.6-2.8 and SPS13.5-1.2 ionomers for \( G'' \) before the peak due to the overlap of the Rouse and ionic dissociation relaxations as discussed above.

The prediction of the reversible gelation model is also shown in Figure 5.1 for comparison, with fitting parameters, Rouse relaxation time \( \tau_0 \) and ionic dissociation time \( \tau_s \), listed in Table 5.1. For \( p < p_c \), the reversible gelation predicted \( G'' \) quite well, but under-predicted \( G' \). The discrepancy in the experimental and predicted \( G' \) was much more evident in NaSPS4.6-1.6 than NaSPS13.5-0.20 due to its much higher \( p \) \( (p > p_g) \). That result may be a consequence of the failure of the model to account for non-effective breakup of the clusters, which may also explain the higher frequency relaxations and broadening of the overall relaxation of the clusters. When \( p \sim p_c \) and \( p > p_c \), the model captured \( G' \) and \( G'' \) for both the SPS4.6 and SPS13.5 ionomers, except that the plateau modulus, \( G_N \), for the former was under-predicted. Since the model assumes all the chain strands (i.e., the chain between
sulfonate groups) are stress-bearing, it predicts a higher plateau modulus than was measured for the SPS13.5 ionomers,\cite{154,160} as a result of network defects, e.g. dangling chains and loops. The lower predicted plateau modulus for the two SPS4.6 ionomers may be due to the uncertainty in the measurement of the sulfonation level, \( p \), since the relaxation close to the gel point is very sensitive to small differences in \( p \). A much better fit was achieved if the value of \( p \) was higher by less than 0.1 mol%.

Table 5.1 Rouse relaxation time (\( \tau_0 \)) and ionic dissociation time (\( \tau_s \)) used for SPS4.6 and SPS13.5 Ionomers at 140°C

<table>
<thead>
<tr>
<th></th>
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<th>SPS4.6-2.5</th>
<th>SPS4.6-2.8</th>
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<tr>
<td></td>
<td>Na</td>
<td>Na K Rb Cs</td>
<td>Na</td>
<td></td>
</tr>
<tr>
<td>( \tau_0 ) (( \mu s ))</td>
<td>1.2</td>
<td>3.8 6.6 6.5 6.5 6.7 19</td>
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</tr>
<tr>
<td>( \tau_s ) (s)</td>
<td>2500 450 250 35 5000</td>
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<table>
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<th></th>
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<th>SPS13.5-0.20</th>
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<tr>
<td></td>
<td>Na</td>
<td>Na K Cs Na</td>
<td></td>
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</tr>
<tr>
<td>( \tau_0 ) (( \mu s ))</td>
<td>20</td>
<td>34 35 38 35 96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tau_s ) (s)</td>
<td>3300 320 21 4340</td>
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</table>

The calculated ionic dissociation times \( \tau_s \) for the different increased with increasing Coulomb energy \( E_c \) of the ion-pair and with increasing \( p \) for both SPS ionomers. However, \( \tau_0 \) was independent of the metal cation, though it increased with increasing \( p \). \( \tau_0 \) for the
SPS13.5 ionomers was an order of magnitude larger than for the SPS4.6 ionomers, which was probably due to higher $T_g$ of the former ($T_g$ of PS13.5 was ~15 °C higher than for PS4.6).

Figure 5.2 shows the shift factors of the SPS4.6 and SPS13.5 ionomers for the master curves in Figure 5.1, and the constants obtained from the WLF equation fit are summarized in Table 5.2. The WLF constants for the ionomers with $p < p_c$ are similar with those of the parent PS, because the relaxation is mainly controlled by the Rouse motions. As a result, the shift factors for the PS13.5 and NaSPS13.5-0.20 ionomer ($p < p_g < p_c$) coincide, though those for the NaSPS4.6-1.6 ionomer ($p_g < p < p_c$) show a slightly stronger temperature dependence at high temperatures than the parent PS4.6 because it is closer to the gel point ($p/p_c = 0.7 > 0.3$ for NaSPS13.5-0.20 ionomer). In general, the WLF constants, $C_1$ and $C_2$, increased with increasing $p$ for both ionomers. For the SPS4.6-2.5 and SPS13.5-0.76 ionomers, where $p \sim p_c$, the WLF constants were relatively insensitive to the choice of the metal cation, changing by less than 1% as the cation changed from Na to Cs (a change of Coulomb energy of 36%), Table 5.2. For the WLF equation, $C_1 \propto 1/f_r$ and $C_2 \propto f_r/\alpha_f$, where $f_r$ is the fractional free volume at $T_r$ and $\alpha_f$ as the free volume expansion coefficient. Thus the increase of WLF constants indicates that both fractional free volume and the volume expansion coefficient decrease with increasing $p$, which can be explained by the densification of polymer due to the strong intermolecular dipolar interactions.

Although the WLF equation fits the shift factors reasonably well, viscoelastic behavior of the ionomers depends upon two relaxation processes that have different
temperature dependences. The first relaxation process is the Rouse relaxation of the precursor chain with the temperature dependence of its relaxation time, $\tau_X = \tau_0 N K^2$, similar to that of PS, though the $\tau_0$ (and $\tau_X$) increases with increasing $p$ (see Table 5.1). The incorporation of ionic groups introduces a second, slower relaxation process, the ionic dissociation of the sulfonate – sulfonate interactions. That relaxation time, $\tau_s$, has a stronger temperature dependence than that of $\tau_X$ (or $\tau_0$) and decreases more rapidly with increasing temperature, as indicated by the much smaller shift factors for the ionomers at higher temperatures than that of PS. The increase of ionic content not only enhances the value of $\tau_s$ (see Table 5.1), but also increase the contribution of ionic dissociation to the overall relaxation of the ionomer. As a result, for SPS4.6 and SPS13.5 ionomer, the temperature dependence of the shift factors becomes much stronger with increasing ionic content, especially at higher temperatures where the shift factor is mainly controlled by the ionic dissociation process.
Figure 5.2 Time-temperature shift factor $a_T$ for SPS4.6 and SPS13.5 ionomers with $T_r = 140^\circ$C. The solid lines show the WLF fits. The shift factors for SPS13.5 and PS13.5 were multiplied by 100 in order to plot the two sets of data on the same scale.

Table 5.2 WLF Constants for PS4.6, PS13.5, SPS4.6, and SPS13.5 ionomers

<table>
<thead>
<tr>
<th></th>
<th>PS4.6</th>
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<td>136</td>
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<td>K 7.8</td>
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<tr>
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5.3.2 Nonlinear behavior: Steady shear flow

The steady shear flow behavior of SPS4.6 ionomers at 170°C with different sulfonate concentration and metal cations is shown in Figure 5.3a. The NaSPS4.6-1.6 ionomer ($p < p_c$) exhibited Newtonian behavior at low shear rates ($\dot{\gamma}$) and shear thinning behavior for $\dot{\gamma} > 10$ s$^{-1}$. The first normal stress coefficient $\Psi_1$ of the NaSPS4.6-1.6 ionomer was only ~0.03 Pa.s$^2$ at $\dot{\gamma} = 40$ s$^{-1}$, indicating weak elasticity. For NaSPS4.6-2.5 ($p \sim p_c$) $\eta$ was constant ($\eta_0 =$ zero shear rate viscosity) at low shear rates, followed by shear thickening behavior for $\dot{\gamma} > 0.025$ s$^{-1}$, and then shear thinning behavior after $\eta$ reached a maximum at $\dot{\gamma} = 0.16$ s$^{-1}$, see orange data in Figure 5.3a. For NaSPS4.6-2.8 ionomer ($p > p_c$), $\eta = \eta_0$ at low shear rate, but decreased rapidly at $\dot{\gamma} > 0.04$ s$^{-1}$ (shown as purple arrow in Figure 5.3a) as a consequence of melt fracture. With reference to the NaSPS4.6-1.6 ionomer, increasing $p$ for the NaSPS4.6-x ionomers increased $\eta_0$ by ~3 and ~4 orders of magnitude and the values of $\Psi_1$ by ~6 and ~8 orders of magnitude for the NaSPS4.6-2.5 and NaSPS4.6-2.8 ionomers, respectively, as a result of higher concentrations of supramolecular crosslinks due to intermolecular dipole-dipole or ion-dipole interactions.

All the SPS4.6-2.5 ionomers exhibited similar steady shear viscosity behavior, with constant $\eta$ at low shear rates and shear thinning at higher shear rates. For the $\Psi_1(\dot{\gamma})$ data, a zero shear rate first normal stress coefficient, $\Psi_{10}$ was not observed and $\Psi_1$ decreased monotonically with increasing shear rate. The decrease of $\Psi_1$ with increasing shear rate was much greater than that of $\eta$. Decreasing Coulomb energy of the ion-pair, $E_c$, decreased $\eta$ and $\Psi_1$, but it also increased the onset shear rate for the shear thinning (i.e., lower
relaxation time), which was due to the lower strength of the intermolecular interactions. Shear thickening behavior was weak, but clear, for the NaSPS4.6-2.5 ionomer, Figure 5.3a, and it became weaker as $E_c$ decreased. A very weak shear thickening was observed for the KSPS4.6-2.5 ionomer, but no shear thickening was observed for the ion-pair with weaker $E_c$, i.e., the Rb and Cs salts. The comparison of the steady state viscosity and the complex viscosity (data not shown here) revealed that the Cox-Merz rule was not obeyed for these ionomers. This result is due to the thermorheological complexity of ionomers, and it is consistent with reports of failure of the Cox-Merz rule for other phase separated melts, such as immiscible blends\textsuperscript{171}, block copolymers\textsuperscript{172} and ionomers\textsuperscript{79, 93, 173}.

The temperature dependence of the steady shear behavior of the NaSPS4.6-2.5 ionomer is shown in Figure 5.3b. $\eta$ and $\Psi_i$ decreased and the onset of shear thinning behavior shifted to higher shear rate with increasing temperature due to weakening of the supramolecular bonds. A shear thickening viscosity followed by shear thinning behavior was observed at all temperatures studied (150$^\circ$C to 200$^\circ$C), though the intensity of the increase in the viscosity decreased with increasing temperature.

Although shear thickening of solutions of associating polymers (such as ionomers) has been reported by various research groups\textsuperscript{161-163, 165-170}, the only report of shear thickening of a polymer melt was that by Weiss and Zhao\textsuperscript{32} for a similar ionomer used in this paper. Four mechanisms have been proposed to explain shear-thickening behavior of associating polymer solutions: 1) shear induced increase of the intermolecular association\textsuperscript{123, 168, 174}, (2) non-Gaussian extension of polymer chains\textsuperscript{167, 175, 176}; (3) anisotropic enhancement of the
association of chain strands in the shear gradient\textsuperscript{163-165}; and (4) repulsive interactions between flowerlike micelles for telechelic polymers\textsuperscript{177}. The fourth mechanism can be discounted for the ionomer melts, because it is improbable that such micelles can be formed in this system. However, the other three mechanisms may explain the shear thickening behavior of the ionomer melts, though other experiments, e.g., rheo-small angle neutron scattering, are needed to resolve whether the phenomenon is due to additional associations or anisotropic chain conformations.
Figure 5.3 Steady shear viscosity and the first normal stress coefficient of: (a) all the SPS4.6 ionomers at 170°C, and (b) NaSPS4.6-2.5 ionomer at various temperatures. The solid lines are drawn only as guides.

The effects of temperature and sulfonation level on the steady shear behavior of the NaSPS4.6 and NaSPS13.5 ionomers are summarized in Figures 5.4-5.6. The viscosity data,
\( \eta(\dot{\gamma}) \) were normalized by the zero-shear viscosity for each ionomer to facilitate comparisons of the behavior at different temperatures. For each molecular weight, \( p \) was varied to compare the behavior of the ionomers below, near and above the gel point, \( p_c \).

Figure 5.4 Effect of temperature on normalized steady shear viscosity for: (a) NaSPS4.6-1.6, (b) NaSPS4.6-2.5, and (c) NaSPS4.6-2.8 ionomers. The inset pictures show the sample fixture at the end of a steady shear experiment. The open symbols represent samples where melt fracture occurred.

At all temperatures, the normalized steady shear viscosity of NaSPS4.6-1.6 (\( p < p_c \)) ionomer exhibited Newtonian behavior at low \( \dot{\gamma} \), followed by shear thinning behavior. The onset of shear thinning shifted to higher \( \dot{\gamma} \) (shorter relaxation time) as the temperature increased. No sign of any instability, such as melt fracture, was observed for any temperature or shear rate, see inset in Figure 5.4a. For NaSPS4.6-2.5 (\( p \sim p_c \)), Figure 5.4b, as the temperature increased the onset of shear thickening shifted to higher \( \dot{\gamma} \) (shorter relaxation time) and the magnitude of the shear thickening became less pronounced, but still observable at temperature as high as 200\(^\circ\)C. No melt fracture was observed during the steady shear experiments, see the inset in Figure 5.4b.
For NaSPS4.6-2.8 \((p > p_c)\), the viscosity remains constant at low \(\dot{\gamma}\), but it decreased when the \(\dot{\gamma}\) exceeded a critical value at which melt fracture was clearly observed. A typical example of the melt fracture behavior is shown in the inset in Figure 5.4c, where the sample exuded from between the cone and plate. The open symbols in Figure 5.4c denote the samples where melt fracture was observed, and except for the small decrease of the viscosity for the experiments where \(T > 200^\circ\text{C}\), melt fracture of the ionomer melts preceded any deviation from constant viscosity of the melt. The melt fracture of SPS ionomer during steady shear is consistent with the catastrophic failure of SPS ionomers during extensional flow. The ionic group associations form an elastic network that is more brittle than an entanglement network in a high molecular weight polymer, since the former lacks the relaxation processes that are provided by diffusional motions of disentanglement of polymer chains.

The steady shear behavior of the NaSPS13.5 ionomers, Figure 5.5a-c, showed qualitatively similar behavior as a function of \(p\) as did the NaSPS4.6 system. For \(p < p_c\) (NaSPS13.5-0.20, Figure 5.5a), the ionomer exhibited shear thinning behavior with no evidence of melt fracture. For \(p \sim p_c\) (NaSPS13.5-0.76, Figure 5.5b), the ionomer melt exhibited shear thinning behavior, and shear thickening also occurred at the lowest temperature used, 150°C. Shear thickening also occurs for KSPS13.5-0.76, but only at 140°C (Figure 5.5d). No melt fracture was observed for any of the other SPS13.5-0.76 ionomers at any temperature (Figure 5.5e).
When the ionic content increased to $p > p_c$ (NaSPS13.5-1.2, Figure 5.5c), however, melt fracture was clearly observed during steady shear flow, see inset picture in Figure 5.5c. The viscosity of the NaSPS13.5-1.2 ionomers was insensitive to shear rate, except when $T > 200^\circ C$, where a relatively small decrease of viscosity occurred above $\dot{\gamma} > 0.004 \text{ s}^{-1}$. The shape of the flow curves where the viscosity decreased appeared unusual in that the viscosity decreased about 10%, but then plateaued until melt fracture occurred at higher $\dot{\gamma}$. The high temperature flow curves for the NaSPS4.6-2.8 sample ($p > p_c$) showed a similar
trend, Figure 5.4c. The reason for that behavior is not known, but it is suspected that there may have been either a flow instability that was not visually observed or, perhaps, some degradation of the polymer occurred at these high temperatures. Note, however, that thermogravimetric analysis (not shown) indicated that no desulfonation should have occurred at the temperatures used in these experiments.

![Figure 5.6 Effect of temperature on the normalized steady shear viscosity for (a) KSPS4.6-2.5, (b) RbSPS4.6-2.5, and (c) CsSPS4.6-2.5 ionomers.](image)

The effect of the cation on the steady shear behavior of SPS4.6-2.5 ionomers is shown by the data in Figures 5.4b and 5.6. These data extend the results reported in ref (32), which reported shear thickening for Li- and Na-salts of a 4000 g/mol SPS ionomer oligomer for \( T > 160^\circ C \). The data in Figure 5.3b and 5.4b confirm the earlier observation of shear-thickening behavior for the Na-salt, and the data in Figure 5.6 show that the phenomenon is also exhibited by the K- and Rb-salts of SPS4.6-2.5, but not the Cs-salt, which has the lowest Coulomb energy.

A general trend revealed in Figures 5.4-5.6 is the shear thickening behavior occurs
only at $p \sim p_c$ and weakens with increasing $T$, increasing molecular weight and lower Coulomb energy of the ion-pairs. Increasing $T$ produces a larger decrease of $\tau_s$ than of $\tau_0$ (or $\tau_X$), which was confirmed in Figure 5.2. The temperature dependence becomes much stronger than the precursor chain at high $T$ where the moduli are governed by the ionic dissociation. Increasing $M$ of the precursor chain enhances the $T_g$ by $\sim 15^\circ C$, leading to a much higher $\tau_0$. The reduction of the Coulomb energy of the ion-pair reduces $\tau_s$. All these effects suggest that the relative values of the ionic dissociation time $\tau_s$ and the Rouse relaxation time of Kuhn segment $\tau_0$ play a major role in whether shear thickening behavior occurs.

The magnitude of shear thickening (i.e., $\eta_{\text{max}}/\eta_0$) as a function of $\tau_s/\tau_0$ for SPS4.6-2.5 and SPS13.5-0.76 ionomers is shown in Figure 5.7. A value of $\eta_{\text{max}}/\eta_0 = 1$ corresponds to no shear thickening. $\tau_s$ and $\tau_0$ at different temperatures were calculated by multiplying the values at $T_r = 140^\circ C$, see Table 5.1, by the WLF shift factors for each relaxation at the other temperatures, Figure 5.8. Recall that TTS failed for these two ionomers, see Figure 5.1, because the ionic dissociation time, $\tau_s$, exhibited a stronger temperature dependence than that of the Rouse relaxation time, $\tau_0$. The temperature dependences of two relaxations were resolved by separately superposing the dynamic modulus data for SPS4.6-2.5 and SPS13.5-0.76 ionomers at the higher frequencies (region I and II in Figure 5.1) to get the temperature dependence of $\tau_0$ and the lower frequency data in the terminal region (region III in Figure 5.1) to get the shift factors for $\tau_s$. The obtained two sets of shift factors are shown in Figure 5.8 and their WLF constants are listed in Table 5.3. For both SPS ionomers, $\eta_{\text{max}}/\eta_0$
increased with increasing $\tau_s/\tau_0$ ratio. For all those data points, $\eta_{\text{max}}/\eta_0$ is roughly proportional to the logarithm of $\tau_s/\tau_0$, indicating that the shear thickening behavior is related to the relative strength of the ionic dissociation to the segmental relaxation.

The effect of the ionic groups on shear thickening data shown here is similar to what Ma and Cooper\textsuperscript{167} reported for hydrophobically end-capped poly(ethylene oxide) polymer solutions, where increasing the association strength of the hydrophobic group (i.e., increasing the chain length of the alkyl end-group), decreasing the molecular weight of the PEO chain, and decreasing the temperature all contributed to a stronger shear thickening behavior. In this system, the hydrophobic end groups tend to form domains in the aqueous media, and those domains serve the same role with the ionic aggregates in the ionomer melts. In fact, the increase of the association strength is similar to the increase of $\tau_s$, the decrease of molecular weight means the decrease of $\tau_0$, and the decrease of $T$ increases $\tau_s/\tau_0$ ratio due to the higher temperature dependence of $\tau_s$. Therefore, we can conclude that a strong shear thickening behavior is favored by a larger contribution of the ionic dissociation, i.e. a larger $\tau_s/\tau_0$ ratio.
Figure 5.7 Temperature dependence of the magnitude of shear thickening for SPS4.6-2.5 and SPS13.5-0.76 ionomers with different metal cations.

Figure 5.8 Time-temperature shift factor $a_T$ of SPS4.6-2.5 and SPS13.5-0.76 ionomers for (a) the Rouse relaxation time $\tau_X$ at $T_r = 140^\circ$C, and (b) the ionic dissociation time $\tau_s$ at $T_r = 190^\circ$C. The solid lines show the WLF fits. The shift factors for SPS13.5-0.76 ionomers were multiplied by 100 for clarity.
Table 5.3 WLF Constants of SPS4.6-2.5 and SPS13.5-0.76 ionomers for the Rouse relaxation time $\tau_X$ at $T_r = 140^\circ C$, and the ionic dissociation time $\tau_s$ at $T_r = 190^\circ C$

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5.3.3 Nonlinear behavior: Startup shear flow

Figure 5.9 shows the viscosity growth function, $\eta^+(t) = \sigma^+(t)/\dot{\gamma}$, and the first normal stress coefficient growth function, $\Psi^+(t) = N^+_1(t)/\dot{\gamma}^2$, where $\sigma^+(t)$ and $N^+_1(t)$ are the shear stress and the first normal stress difference, respectively, for the NaSPS4.6 ionomers upon startup of shear flow for various shear rates. Also shown by the solid curves in Figure 5.9 are the LVE limit predictions calculated from Equations (5.1) and (5.2),

$$\eta^+(t) = \int_0^t G(t') \dot{\gamma} dt'$$  \hfill (5.1)

$$\Psi^+_1(t) = 2 \int_0^t G(t') \dot{\gamma}^2 dt'$$  \hfill (5.2)

where $G(t)$ is relaxation modulus calculated from the dynamic modulus using the iteration method developed by Watanabe et al.\textsuperscript{178, 179}
For $p < p_e$ (NaSPS4.6-1.6, Figure 5.9a), $\eta^+(t)$ at low shear rates, $\dot{\gamma} = 2.5$ s$^{-1}$, is coincident with the LVE envelope. The viscosity shows a monotonic increase to a steady state value within $\approx 0.3$ s. For $\dot{\gamma} > 2.5$ s$^{-1}$, $\eta^+(t)$ exhibits an overshoot before reaching steady state. Similar viscosity (stress) overshoots are typically observed for entangled polymer melts$^{180,181}$, where the maximum and longer time response are related to the chain stretch and convective constraint release, respectively.$^{182}$ However, these oligomeric ionomers are below their entanglement molecular weight. A possible explanation for the stress overshoot in the ionomers is yielding of the supramolecular crosslinks due to shear-induced breakup of the ionic association. When $\dot{\gamma} \geq 40$ s$^{-1}$, the stress overshoot was followed by a weak stress (viscosity) minimum before the viscosity achieved steady state. The overshoot and undershoot became more apparent as the shear rate increased. Similar behavior was observed for the NaSPS4.6-1.6 ionomer at other temperatures ($140^\circ C \leq T \leq 160^\circ C$) and for NaSPS13.5-0.20 (Figure 5.12d), and also for entangled PS$^{183}$ melts. The stress undershoot following the overshoot has been attributed to the tumbling of individual polymer chains at high shear rates for entangled polymers.$^{183}$ Therefore, the stress undershoot for the NaSPS4.6-1.6 ionomer may also be ascribed to the tumbling of the large clusters, whose sizes are similar to that of entangled polymer chains.

The first normal stress coefficient function, $\Psi_1^+(t)$, of NaSPS4.6-1.6 (Figure 5.9d) exhibited a monotonic increase when $\dot{\gamma} \leq 10$ s$^{-1}$, and a weak overshoot when $\dot{\gamma} \geq 25$ s$^{-1}$. The linear envelope calculated from the dynamic modulus is much higher than the $\Psi_1^+(t)$ at short times possibly due to the instrumental error at this extremely low normal stress.
levels. The small values of $\Psi^+(t)$ is consistent with the limited data of normal stress coefficient obtained in the steady shear experiment (Figure 5.3a), and in accordance with the absence of supramolecular structure in NaSPS4.6-1.6 ionomer (Figure 5.1a).

Figure 5.9 Shear viscosity growth function $\eta^+(t)$ and the first normal stress coefficient growth function $\Psi^+(t)$ measured at various shear rates for (a) and (d) NaSPS4.6-1.6, (b) and (e) NaSPS4.6-2.5, (c) and (f) NaSPS4.6-2.8 at 170 °C. The solid curves correspond to the LVE limit calculated from the dynamic modulus (Eqs 5.1-5.2).

For $p \sim p_c$ (NaSPS4.6-2.5, Figure 5.9b), $\eta^+(t)$ increased monotonically and it coincides with the LVE envelope when $\dot{\gamma} \leq 0.01 \text{ s}^{-1}$ (the data at $\dot{\gamma} < 0.01 \text{ s}^{-1}$ wasn’t shown for clarity). For higher shear rates, the steady state viscosity increases weakly with the shear rate until $\dot{\gamma} = 0.16 \text{ s}^{-1}$ (data with $0.01 \text{ s}^{-1} < \dot{\gamma} < 0.16 \text{ s}^{-1}$ was not shown here). This increase of steady state viscosity is consistent with the observation in Figure 5.3. However, at $\dot{\gamma} \leq 0.16 \text{ s}^{-1}$, there exists a fluctuation in the $\Psi^+(t)$ data due to the small value of the first normal stress.
difference $N_1^+$, making it harder to determine whether the steady state normal stress coefficient also exhibit an increase with increasing shear rate. The viscosity (stress) overshoot becomes apparent at $\dot{\gamma} \geq 0.4 \text{ s}^{-1}$, where the viscosity before the yielding exhibits a much steeper increase than that of the linear envelope, which is due to strain-hardening similar to what is often observed in shear thickening solutions.\textsuperscript{163, 165, 166} The $\Psi_1^+(t)$ curve only shows a very weak stress overshoot at $\dot{\gamma} \geq 0.4 \text{ s}^{-1}$.

The $\eta^+(t)$ and $\Psi_1^+(t)$ curves of NaSPS4.6-2.8 ($p > p_c$) ionomer are shown in Figure 5.9c and f, respectively. For $\dot{\gamma} \leq 0.025 \text{ s}^{-1}$, the $\eta^+(t)$ curves agreed well with the LVE envelope and the steady state values for viscosity were the same. When $\dot{\gamma} = 0.04 \text{ s}^{-1}$, a small stress overshoot was observed, after the overshoot the viscosity decreased gradually before a more rapid decrease occurring at $t = 100\text{s}$ (shown as black arrow), where melt fracture was visually observed from the sample. The strain hardening was not observed. Unlike the other two ionomers, the $\Psi_1^+(t)$ curve of NaSPS4.6-2.8 ionomer also deviates from the linear envelope and remains nearly constant during the startup shear. The reason for this abnormal trend of $\Psi_1^+(t)$ is still unknown, and it might be related to the breakup and recovery of the physical ionic network, where a small normal stress could lead to a quite large $\Psi_1^+(t)$ due to the considerably small values of shear rate.

Strain hardening was observed when the ionomer was close to the gel point ($p \sim p_c$). In order to further understand this phenomenon the startup shear flow behavior of the NaSPS4.6-2.5 ionomer ($p \sim p_c$) was measured at three different temperatures, 180°C, 190°C and 200°C, Figure 5.10. The trends in the $\eta^+(t)$ data for the three temperatures were
similar to those discussed above for the data at 170°C. At lower shear rates $\dot{\gamma} \leq \dot{\gamma}_{\text{max}}$ (where $\dot{\gamma}_{\text{max}}$ is defined as the shear rate where the steady shear viscosity $\eta$ attained its maximum value), the viscosity curves agreed well with the LVE envelope prediction and the steady state values of the $\eta^+(t)$ increased with increasing shear rate. At the higher shear rates ($\dot{\gamma} > \dot{\gamma}_{\text{max}}$), stress overshoot and strain hardening were clearly observed. The magnitude of strain hardening decreased with increasing temperature, which is consistent with the decreasing value of the ionic dissociation time $\tau$. The $\Psi^+(t)$ data in Figure 5.10 for NaSPS4.6-2.5 are also similar to the 170°C data shown in Figure 5.9, exhibiting no nonlinearity at $\dot{\gamma} \leq \dot{\gamma}_{\text{max}}$ and a overshot at $\dot{\gamma} > \dot{\gamma}_{\text{max}}$.

Figure 5.10 Shear viscosity growth function $\eta^+(t)$ and the first normal stress coefficient growth function $\Psi^+(t)$ of the NaSPS4.6-2.5 ionomer measured at various temperatures: (a) and (d) 180 °C, (b) and (e) 190 °C, (c) and (f) 200 °C. The solid curves represent the linear viscoelastic data calculated from dynamic modulus.
Figure 5.11 compares the viscosity growth functions $\eta^+(t)$ at 170°C for K, Rb and Cs-salts of SPS4.6-2.5. Like the NaSPS4.6-2.5 data in Figure 5.9, the viscosity curves lie on the LVE envelope at low shear rates, $\dot{\gamma} < \dot{\gamma}_{\text{max}}$, and stress overshoot occurred at the higher shear rates, $\dot{\gamma} \geq \dot{\gamma}_{\text{max}}$. In particular, KSPS4.6-2.5 ionomer exhibits a weak shear thickening as the steady state values of $\eta^+(t)$ reaches the maximum at $\dot{\gamma} = \dot{\gamma}_{\text{max}} = 1 \text{ s}^{-1}$ (only two shear rates were shown for clarity), which is consistent with the observed in Figure 5.3a. Strain hardening became weaker with decreasing $E_c$, and almost disappeared for the Cs-salt. Strain hardening and shear thickening weakened with increasing of temperature and decrease of $E_c$ of the ion-pair, which is due to decreases of $\tau_s$.

![Figure 5.11](image)

**Figure 5.11** Shear viscosity growth function $\eta^+(t)$ measured at 170 °C for (a) KSPS4.6-2.5, (b) RbSPS4.6-2.5, and (c) CsSPS4.6-2.5 ionomers. The solid curves correspond to the linear viscoelastic data calculated from dynamic modulus.

The SPS13.5 ionomers showed similar behavior in startup shear flow at 170°C as that of the SPS4.6 ionomers. Shear thinning behavior was observed when $p < p_c$, and melt fracture occurred when $p > p_c$ (Figure 5.12d-e). However, close to the gel point ($p \approx p_c$; the SPS13.5-0.76 ionomers), the stress growth behavior differed from that of the SPS4.6
ionomers. For all three salts, almost no strain hardening was observed, Figure 5.12a-c, and no shear thickening behavior occurred. That result further supports the hypothesis that the shear thickening and the strain hardening behavior in these ionomers are related, and that the two phenomena occur only occur at high ratios of $\tau_s/\tau_0$. Note that for the higher molecular weight ionomers, the magnitude of $\tau_0$ increased by an order of magnitude, but $\tau_s$ was almost the same as for the SPS4.6 ionomers.

Figure 5.12 Shear viscosity growth function $\eta^+(t)$ of (a) NaSPS13.5-0.76, (b) KSPS13.5-0.76, (c) CsSPS13.5-0.76, (d) NaSPS13.5-0.20, and (e) NaSPS13.5-1.2 at 170 °C. The solid curves correspond to the linear viscoelastic data calculated from the dynamic modulus.

The observations of weak shear-thickening followed by shear-thinning behavior, strain-hardening accompanying shear-thickening, and almost no observable nonlinearity
for $\Psi_1$ or $\Psi_1^+(t)$ at the shear rate range of shear thickening are similar to those reported by Watanabe and coworkers\textsuperscript{163-165} for the non-linear rheology of hydrophobically end-modified ethoxylated urethane (HEUR) solution. Those authors observed that shear thickening occurred only for a solution with sparse physical network, meaning that the network has yet formed but the gel concentration is low, leading to super-bridged network strands. Watanabe and coworkers argued that if non-Gaussian deformation or shear-induced change from intra- to inter-chain aggregation controls the shear thickening, it would lead to nonlinearity of $\Psi_1$ and $\Psi_1^+(t)$ as well\textsuperscript{163} The absence of nonlinearity for $\Psi_1$ encourages them to propose a single chain type transient network model (SCT model)\textsuperscript{164} In SCT model, a dense, well-percolated network is formed in the concentrated solution with individual polymer chain as chain strand, while only a sparse network exists in the dilute solution with chain strands as so called superbridges, defined as branched strands that formed by several precursor chains through the association between hydrophobic end groups\textsuperscript{164, 165}. At high concentration, the micellar cores, formed by the association of hydrophobic end groups, behave like typical physical crosslinks. In contrast, at low concentration, the micellar cores can serve as crosslinks and more dominated as association sites in the superbridges (chain strands for the sparse network)\textsuperscript{164, 165}. The nonlinear rheological behavior was found to be highly dependent on the dissociation/association of the micellar cores in the superbridges, and the shear thickening was attributed to the anisotropic distribution of those micellar cores in the shear gradient direction.

The structural feature of HEUR solution is quite similar to that of SPS ionomers. At
$p > p_c$, a well-defined ionic network formed with the chain strands mainly formed by the chain segments between ionic groups. The average size of the network strands decreasing with increase of $p$ from infinitely large at $p \sim p_c$ to the size of precursor chain at $p \sim 2p_c$. In particular, at $p \sim p_c$, only an infinitely small amount of percolated network exists, where the chain strands are ionic clusters, defined as branched chains connected by the ionic aggregates.\textsuperscript{184} Considering the similar nature of the ionic aggregates with micellar cores, the SCT model could also explain the shear thickening behavior of the SPS ionomers close to the gel point. Nevertheless, the magnitude of shear thickening in the ionomer melts is much weaker than that observed in solution\textsuperscript{165, 167}. The reason for this difference is probably attributed to the high bulk viscosity and the small fraction of clusters that play active role during shear thickening.

For typical entangled polymers, the strain $\gamma_{\text{max}}$, defined as the strain at the peak of the viscosity growth curves, is $\sim 2.3$ when the Rouse Weissenberg number $W_iR$, the product of shear rate and Rouse time of the entanglement strands, is less than 1, and increases with increasing $W_iR$ when $W_iR > 1$.\textsuperscript{180, 181, 183, 185} In the oligomeric SPS ionomer system, the Weissenberg number, $W_i$, instead, was defined as the product of shear rate and terminal relaxation time, i.e. the effective breakup time of the branched clusters, as those branched clusters serve as strands of the ionic network. When $W_i < 1$, the ionomer chains have enough time to re-equilibrate and relax. In contrast, for $W_i > 1$, the branched clusters are stretched and at some critical strain, the aggregates break-up, which produces the overshoot in the viscosity. Figure 5.13 plots the strain at the viscosity maximum during startup shear
flow against $Wi$ for the ionomers near the gel point ($p \sim p_c$), SPS4.6-2.5 and SPS13.5-0.76. For both ionomers, $\gamma_{\text{max}} \sim 2$ when $Wi < 1$, and then increases with increasing $Wi$. $\gamma_{\text{max}}$ increased faster with $Wi$ for the SPS13.5-0.76 ionomers than for SPS4.6-2.5, which may be a consequence of higher molecular weight ($M_w = 13.5k$ vs. $M_w = 4.6k$). Although both ionomers contain around one ionic group per chain on average, the chain segments between ionic groups are longer for SPS13.5-0.76 ionomers, which allows a higher degree of deformation during the shear. The value of $\gamma_{\text{max}}$ decreased with decreasing Coulomb energy, which is a consequence of the weaker supramolecular bonds that break at lower strain.

![Figure 5.13 Value of the strain corresponding to the peak in viscosity at 170°C for SPS4.6-2.5 (filled symbols) and SPS13.5-0.76 (open symbols) ionomers against $Wi$.](image-url)

Figure 5.13 Value of the strain corresponding to the peak in viscosity at 170°C for SPS4.6-2.5 (filled symbols) and SPS13.5-0.76 (open symbols) ionomers against $Wi$. 
5.4 Conclusions

This study investigated the nonlinear viscoelasticity of sulfonated polystyrene oligomers with degree of sulfonation below, close to, and above the gel point. When the degree of sulfonation is below the gel point, only shear thinning was observed. While above it, melt fracture occurs. Only when the degree of sulfonation is close to the gel point, shear thickening emerges. The magnitude of shear thickening decreases with the increase of temperature, $M$ of PS precursor and the Coulomb energy of the ion pair, all leading to less contrast between Rouse time $\tau_0$ and the ionic dissociation time $\tau_s$. In the startup shear, pronounced stress overshot and strain hardening were observed, and only observed, when ionomer close to the gel point. The shear thickening in viscosity was accompanied by the absence of nonlinearity in the first normal stress difference coefficient. Though the mechanism for the shear thickening is still under debating, those observations would definitely contribute to the understanding of the non-linear rheology of the random ionomers.
CHAPTER VI

RHEOLOGICAL AND DIELECTRIC BEHAVIOR OF PARTIALLY NEUTRALIZED
OLIGOMERIC SULFONATED POLYSTYRENE IONOMERS

6.1 Introduction

Polymers containing small amount, typically less than 15 mol%, of covalently attached ionic groups are often called ionomers. Those polar ionic groups tend to form nanometer-sized aggregates in the low dielectric constant medium because of their strong dipolar or ionic interactions. The physical and mechanical properties of ionomers are significantly modified by the presence of ionic aggregates as physical crosslinks. Therefore, ionomers have been widely used in the past decades as polymer blends compatibilizers, packaging films, shape memory polymers, and self-healing materials etc.

The dynamics of ionomers is strongly related to the dissociation of ion pairs from the ionic aggregates. The effects of the ionic content and cation type on the linear and nonlinear rheological behavior of ionomers have been reviewed by Register and Prud’homme. However, limited studies have been performed so far to understand the role of neutralization degree on the dynamics of ionomers. For instance, Bonotto et al. found that the mechanical properties of poly(ethylene-co-acrylic acid) ionomers (PEAA) mainly depends on the degree of neutralization rather than the type of
metal cations. Increasing neutralization degree increases the modulus and decreases the melt index for all the metal salts of PEAA. Register et al. found that the terminal relaxation time and zero-shear viscosity of poly(ethylene-co-methacrylic acid) (PEMA) ionomers increased with the increase of neutralization degree for ionomers neutralized by monovalent and divalent metal cations. The unneutralized acid groups (free acid groups) exhibited a plasticization effect on the ionic interaction, significantly facilitating the ion-hopping process, especially for ionomers with low neutralization degrees. Despite those studies, no rheological data with neutralization degree of 90%-100% has been reported for this entangled PEMA ionomer system. Similar with PEMA ionomers, the melt viscosity was found to increase with the neutralization degree for other ionomers such as sulfonated polystyrene (SPS), carboxylated poly(methyl methacrylate) and poly(styrene-co-methacrylate) ionomers. In particular, Lundberg et al. discovered that the increase of melt viscosity for SPS ionomers became rather steep above 90% neutralization, however, the reason for this transition of melt viscosity is still unknown.

For all the studies discussed above, the ionomer chains are highly entangled. One serious drawback of using entangled ionomers is that the effect of the ionic interactions on the rheology is often complicated by the presence of chain entanglements. In order to isolate the effect of ionic interaction from the chain entanglement, oligomeric sulfonated polystyrene (SPS) ionomers have been widely used as a model system to study the dynamics of random ionomers. In our previous studies, the effects of sulfonation degree

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and metal cation on the shear and extensional rheology of ionomer melts have been extensively investigated.\textsuperscript{32, 80, 85, 154, 155, 160} The gel point, $p_c$, was determined as one ionic group per chain on average for both neat ionomers and ionomer blends.\textsuperscript{154, 160} Below the gel point, the ionomers show longer terminal relaxation than PS precursor due to the increased chain friction, whereas, no plateau was observed in the storage modulus.\textsuperscript{160} Close to the gel point, two power law regions corresponding to the mean-field and critical percolations start to emerge.\textsuperscript{154, 160} Above the gel point, a clear plateau in the storage modulus occurs with the plateau modulus independent of the cation type but increases with the ionic content.\textsuperscript{32, 80, 154, 160} The binary ionomer blends show similar LVE behavior but slightly different relaxation spectrum with that of neat ionomers due to the different distribution of ionic groups.\textsuperscript{160} The reversible gelation model, developed through modifying the mean field theory of Rubinstein and Semonov,\textsuperscript{136, 137} predicts quite well the LVE behavior of both neat ionomers and ionomer blends with only two parameters, the Rouse relaxation time of the Kuhn segment $\tau_0$ and the ionic dissociation time $\tau_s$. In particular, the mixing of two different alkaline cations was found to follow a linear additive rule, i.e. the ionic dissociation frequency of the blend is the linear addition of the ionic dissociation frequency of two component cations.\textsuperscript{160}

Herein, three SPS ionomers, prepared from the same PS precursor ($M_w = 13.5k$ g/mol), with different degrees of sulfonation ($p = 1.2, 1.5$ or 2.7 mol\%\) were selected to understand the effect of neutralization degree on the LVE and steady shear behavior. The LVE behavior of the partially neutralized ionomer was also compared with the blends of unneutralized
ionomer (acid derivative) and fully neutralized ionomer containing similar cation content. The similar LVE behavior for these two systems suggests that the ionic aggregates are composed of both sulfonic acids and alkali sulfonates. Dielectric relaxation spectroscopy showed that the dielectric constant of ionomers increases with the content of sulfonic acid. Therefore, we propose that the presence of the acid groups does not only plasticizing the aggregate, but also softens the electrostatic interaction between ionic groups. Incorporating this latter effect enables us to better predict the LVE behavior, in particular at high degree of neutralization where the viscosity increases significantly.

6.2 Experimental section

This section described the synthesis and the characterization of the rheological and dielectric behavior of partially neutralized SPS ionomers.

6.2.1 Materials

Oligomeric polystyrene (PS13.5), $M_w = 13.5k$ g/mol, with narrow polydispersity (PDI < 1.06) was purchased from Pressure Chemical Co. (Pittsburgh, PA), and sulfonated in a 1,2-dichloroethane (DCE) solution using acetyl sulfate. Acetyl sulfate, freshly prepared through adding concentrated sulfuric acid into 60 mol% excess of acetic anhydride in DCE at 0°C, was added into a ~10wt% PS/DCE solution (~200ml) at ~50°C under constant stirring in ~1min. After 1h, the reaction was terminated by adding ~2ml of 2-propanol. Note that the substitution of hydrogen to sulfonic acid group occurs randomly at the para-position of the phenyl ring. The sulfonated polystyrene (SPS) was precipitated in boiling de-ionized water, washed three times with di-ionized water, dried in air at 70°C for 1 day,
and finally dried at 120°C in a vacuum oven for 1 week. The sulfonation level was
determined by sulfur elemental analysis at Robertson Microlit Analysis (Madison, NJ).

Three different SPS were prepared with degrees of sulfonation of 1.2, 1.5 and 2.7
mol%, which corresponds to 1.6, 1.9, and 3.5 ionic groups per chain on average,
respectively. However, those SPS samples include a distribution of chains with different
ionic groups due to the random sulfonation process. Partially or fully neutralized SPS
was prepared by adding predetermined amount of sodium hydroxide/methanol solution
into a ~15wt% solution of SPS acid derivative in a 90/10 (v/v) mixture of toluene and
methanol. After 30min, the neutralized SPS was collected following the procedures as
described above for SPS. In particular, for fully neutralized SPS ionomers, 50 mol% excess
of sodium hydroxide was used to ensure a complete neutralization. The percentage of
neutralization degree was calculated from the sodium content, which was measured by
sodium element analysis at Robertson Microlit Analysis (Madison, NJ). The binary blends
used in this study were prepared by blending predetermined amount of fully neutralized
SPS and SPS acid derivative in mixed solvent of 90/10 (v/v) toluene and methanol. The
blend samples were isolated using the same procedures for the neat ionomers. The sample
nomenclature used hereafter is Na\textsubscript{p}x(b), where Na denotes the cation, p represents the
degree of sulfonation in mole percentage (mol%), x is neutralization degree in mol
percentage (mol%), and b, if exists, denotes the blend sample.

6.2.2 Materials characterization

Both small amplitude oscillatory shear and steady shear measurements were
conducted in a TA Instruments ARES-G2 rheometer. Dynamic frequency sweeps were carried out at a temperature range of 100-250°C and a frequency range of 0.16-250 rad/s with either 25 or 8mm parallel plates. All dynamic measurements were performed within the linear viscoelastic regime as determined from the strain sweep. Considering the glass transition temperature for the SPS matrix varies by only 4 °C, time-temperature-superposition (TTS) master curves were constructed at the same reference temperature $T_r = 140 \degree C$ for comparison. Steady shear experiments were performed over a temperature range of $T = 150 - 200^{\circ}C$ and a shear rate range of 0.0001 - 1000 s$^{-1}$ using a cone and plate fixture with a diameter of 25 mm and a cone angle of 0.04 rad.

Dielectric relaxation spectroscopy (DRS) measurements were performed in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer. Samples were loaded on a freshly polished brass electrode with a diameter of 25mm and then quickly heated up to 180-200°C in vacuum. After annealing the sample for more than 12 hours, the top brass electrode with a diameter of 20mm was loaded. This step degased the sample effectively. A gap of 1mm was kept between the top and bottom electrodes by silica spacers. Before the DRS measurements, the samples were annealed in the instrument at 200°C or higher $T$ for half an hour under nitrogen for drying. Isothermal frequency sweeps were conducted in 10K steps from 200°C or higher $T$ downwards to 80°C with the frequency ranging from $10^7$ Hz to $10^{-2}$ Hz.

6.3 Results and discussion

This section investigated the effect of neutralization degree on the linear rheological
behavior of SPS ionomers, and then compared it with their dielectric behavior.

6.3.1 Linear viscoelastic behavior

The gel point for an random ionomer was determined to $p_c = 100\text{mol}\%/(N-1)$, where $N$ is the degree of polymerization.\textsuperscript{154} For SPS13.5 ionomers, $p_c = 0.78$ mol\%. Above the gel point ($p > p_c$), a percolated ionic network (gel) was formed in the ionomer, and the fraction of the gel increases with $p$ until the system is completely gelled at $p = 2p_c$.\textsuperscript{154} In this contribution, SPS13.5 ionomers with three different degrees of sulfonation were investigated, where the first two ionomers, $p = 1.2$ and 1.5 mol\%, are mixtures of sol and gel ($p_c < p < 2p_c$), and the third ionomer, $p = 2.7$ mol\%, is a complete gel ($p > 2p_c$).

Figures 6.1 shows the master curves of storage modulus, $G'$, and loss modulus $G''$, at $T_r = 140$ °C for different Na1.2-\textit{x} ionomers ($p_c < p < 2p_c$). When $x \leq 76$, TTS works quite well and no plateau in the storage modulus was observed for all ionomers, despite that the Na1.2-76 ionomer has a higher Na content (= 0.91 mol\%) than the gel point $p_c$ (= 0.78 mol\%). This indicates that the presence of extra unneutralized acid groups could weaken the ionic dissociation behavior\textsuperscript{100} and delay the appearance of the modulus plateau. For all the Na1.2-\textit{x} ionomers with $x \leq 76$, $G'$ and $G''$ exhibits typical Rouse behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{1/2}$, before the terminal relaxation. The increase of neutralization degree delays the terminal relaxation and expands the Rouse region to lower frequencies due to the stronger ionic interaction of Na sulfonates than acid groups. When $x \geq 89$, a plateau in $G'$ occurs, and this plateau becomes more pronounced with higher $x$. However, the increase of neutralization degree, i.e. increasing fraction of Na cation, does not affect
the plateau modulus. This phenomenon is consistent with our previous observations that
the plateau modulus of SPS ionomers is independent of the alkali metal cation.\textsuperscript{32, 80, 154, 160}
Furthermore, it also demonstrates that the acid groups may also participate in the formation
of ionic network like the alkali cations. For ionomers with $x \geq 89$, TTS works well for $G'$
but fails in the valley of $G''$ because of the overlap of two relaxation processes, the ionic
dissociation and the Rouse relaxation, with different temperature dependences.\textsuperscript{32, 80, 85, 154, 160}

Compared to PS13.5 precursor, the incorporation of sulfonic acid groups shifts the
terminal relaxation to lower frequency by several times due to the ionic interactions
between acid groups. The conversion of sulfonic acid into Na sulfonate, i.e. the increase of
neutralization degree, $x$, from 0 to 100, further delays the terminal relaxation by as high as
5 orders of magnitude. This delay of terminal relaxation strongly depends on the
neutralization degree, $x$, and exhibits a clear transition at $x = 89$. When $x < 89$, the increase
of $x$ from 0 to 89 delays the terminal relaxation by around 2 orders of magnitude, while
similar delay is achieved by increasing $x$ by only 11 (from $x = 89$ to $x = 100$). Such transition
of terminal relaxation was also observed in the LVE behavior of Na1.5-$x$ ionomers, where
the transition occurs at $x = 85$ (Figure 6.2).

The effect of neutralization degree on the master curves of Na2.7-$x$ ionomers ($p > 2p_c$)
was shown in Figure 6.3. Similar to Na1.2-$x$ ionomers, the terminal relaxation is shifted to
lower frequency upon the increase of neutralization degree. However, this shift is much
stronger in Na2.7-$x$ ionomers due to their higher sulfonation degree. The presence of the
unneutralized acid groups significantly delays the appearance of the plateau in $G'$. The modulus plateau starts to emerge at $x = 50$, where the ionomer contains a Na content ($p_{Na} \approx 1.4$ mol%) almost twice as large as the gel point $p_c$. With the increase of neutralization degree, the plateau modulus remains the same, while the breadth of the modulus plateau increases gradually due to the increased ionic interaction. TTS works well for Na2.7-$x$ ionomers with $x \leq 40$, but starts to fail in the valley of $G''$ when $x \geq 50$ due to the overlap of ionic dissociation and Rouse relaxation as discussed above.\textsuperscript{32, 80, 85, 154, 160} Similarly, a transition in the terminal relaxation was clearly observed. When $x > 81$, increasing $x$ by \approx 20 delays the terminal relaxation by 3 orders of magnitude, while similar delay requires an increase of $x$ by 81 (from 0 to 81).
Figure 6.1 Frequency dependence of storage and loss moduli, $G'$ and $G''$, master curves at $T_r = 140 \, ^{\circ}C$ for Na1.2-x ionomers. The solid curves are the model predictions.
Figure 6.2 Frequency dependence of $G'$ and $G''$, master curves at $T_r = 140 \, ^\circ\text{C}$ for Na1.5-x ionomers. The solid curves are the model predictions.

For all three types of Na$p$-x ionomers, the plateau modulus is independent of neutralization degree for all three ionomers, which indicates that the acid groups also contribute to the formation of ionic network like metal sulfonates (Figures 6.1-6.3). In addition, the increase of terminal relaxation time becomes rather steep when $x > 80$ for all
three ionomers. This phenomenon is in accordance with a previous study of entangled SPS by Lundberg et al.,\textsuperscript{107} where the slope of melt viscosity against neutralization degree exhibited a rapid increase at around $x = 90$. However, similar observation was not reported in PEMA ionomer system due to the absence of experimental data with $x > 90$.\textsuperscript{64,100}

Figure 6.3 Frequency dependence of storage and loss moduli, $G'$ and $G''$, master curves at $T_r = 140$ °C for Na2.7-$x$ ionomers. The solid curves are the model predictions.

The temperature dependence of the shift factors used to construct the $G'$ and $G''$ master
curves in Figures 6.1-6.3 is shown in Figure 6.4. For all three ionomers, the shift factors show a stronger temperature dependence for ionomers with higher neutralization degrees. Those constants used to fit the Williams-Landel-Ferry (WLF) equation are listed in Tables 6.1, 6.2, and 6.3 for Na1.2-x, Na1.5-x and Na2.7-x ionomers, respectively. For all ionomers, $C_1$ and $C_2$ increase with increasing $x$. According to the free volume theory, $C_1$ is proportional to $1/f_r$ and $C_2$ is proportional to $f_r/\alpha_f$, where $f_r$ is the fractional free volume at $T_r$, and $\alpha_f$ is the free volume expansion coefficient. For Na1.2-x ionomers, the changes in the WLF constants $C_1$ and $C_2$ indicate that the fractional free volume $f_r$ and the volume expansion coefficient $\alpha_f$ decreased by ~20% and ~35%, respectively, as $x$ increases from 0 to 100. While for Na2.7-x ionomers increasing $x$ from 0 to 100 results in a larger decrease of $f_r$ and $\alpha_f$ by ~30% and ~50%, respectively, due to their higher sulfonation degree. Similar trend was also observed in Na1.5-x ionomers (Figure 6.4b and Table 6.2), where the decrease of $f_r$ and $\alpha_f$ lies between both ionomers. Those changes in the fractional free volume and the volume expansion coefficient are probably the consequence of the densification of ionomers chains due to the strong ionic interaction.
Figure 6.4 Time-temperature shift factor $a_T$ with respect to $T - T_r$ for (a) Na1.2-x, (b) Na1.5-x, and (c) Na2.7-x ionomers. The solid lines show the WLF fit.
Table 6.1 WLF Constants for Na1.2-x ionomers.

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<tr>
<th>$x$</th>
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<th>56</th>
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<th>89</th>
<th>92</th>
<th>96</th>
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<td>7.6</td>
<td>8.2</td>
<td>8.6</td>
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<td>99</td>
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<td>106</td>
<td>105</td>
<td>123</td>
<td>121</td>
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Table 6.2 WLF Constants for Na1.5-x ionomers.

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<th>38</th>
<th>56</th>
<th>75</th>
<th>85</th>
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<td>8.2</td>
<td>8.7</td>
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<td>103</td>
<td>107</td>
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Table 6.3 WLF Constants for Na2.7-x ionomers.

<table>
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<th>40</th>
<th>50</th>
<th>71</th>
<th>81</th>
<th>91</th>
<th>95</th>
<th>100</th>
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<tbody>
<tr>
<td>$C_1$</td>
<td>7.8</td>
<td>8.1</td>
<td>8.7</td>
<td>9.3</td>
<td>10.0</td>
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<td>115</td>
<td>116</td>
<td>120</td>
<td>124</td>
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</tbody>
</table>

In order to further investigate the effect of unneutralized acid groups, Figure 6.5 compares the LVE behavior of partially neutralized ionomers with that of fully neutralization ionomer containing similar Na content: a) $p_{Na} \sim p_c$ for Na0.76-100 ($p_{Na} = 0.76$ mol%), Na1.5-56 ($p_{Na} = 0.84$ mol%) and Na2.7-30 ($p_{Na} = 0.81$ mol%); and b) $p_c < p_{Na} < 2p_c$ for Na1.2-100 ($p_{Na} = 1.2$ mol%) and Na2.7-50 ($p_{Na} = 1.4$ mol%) ionomer. For the
first group (Figure 6.5a), there is a significant difference in the LVE behavior between partially neutralized ionomers and fully neutralized ionomers. The dynamic modulus of Na0.76-100 ionomer shows distinct critical percolation behavior with $G' \sim G'' \sim \omega^{2/3}$, while such power law relaxation is absent in both Na1.5-56 and Na2.7-30 ionomers probably due to the presence of unneutralized acid groups. In addition, the Na2.7-30 ionomer has a slightly higher dynamic modulus in the Rouse region ($G' \sim G'' \sim \omega^{1/2}$), but lower modulus in the terminal region than Na1.5-56 ionomer as the former contains a higher amount of unneutralized acid groups (1.9 mol% vs 0.7 mol%). The existence of the extra acid groups delays the Rouse relaxation, but significantly promotes the ionic dissociation and terminal relaxation. For the second group (Figure 6.5b), the partially neutralized ionomer (Na2.7-50) shows a very weak modulus plateau, while the fully neutralized ionomer (Na1.2-100) exhibits a well-defined plateau which spans as large as 3 orders of frequency despite its relatively lower Na content (1.2 mol% vs 1.4 mol%). This is consistent with the trend observed in Figures 6.1-6.3 that the presence of unneutralized acid groups delays the appearance the modulus plateau. These differences between partially neutralized and fully neutralized ionomers demonstrate that the acid groups could weaken the ionic interaction between Na sulfonates, thus promoting the ionic dissociation. However, Tierney and Register\textsuperscript{100} found that the presence of extra acid groups does not significantly affect the viscosity of two PEMA ionomers containing different ionic content but similar Na content, which might be attributed to the existence of chain entanglement and long chain structure in these two ionomers.
Figure 6.5 Comparison of LVE behavior for partially neutralized ionomers and fully neutralized ionomers with similar Na contents at 140°C. The Na content was shown in the bracket of the legend.

The LVE behavior of three partially neutralized ionomers were fitted with our previously developed reversible gelation model, where the effect of neutralization degree was quantified by one of the two parameters, the ionic dissociation time $\tau_s$. Figure 6.6 summarizes the values of the Rouse relaxation time of an Kuhn segment ($\tau_0$) and the ionic dissociation time ($\tau_s$) obtained from the model fitting shown in Figures 6.1-6.3. For all the Nap-$x$ ionomers, the $\tau_0$ increases with the neutralization degree $x$ probably due to the decreased chain mobility with increasing fraction of Na sulfonates (Figure 6.6a). The increase of segmental relaxation $\tau_0$ with increasing $x$ is consistent with the decrease of fractional free volume and the volume expansion coefficient discussed above (Tables 6.1-6.3). The ionic dissociation time $\tau_s$ also increases with $x$ because of the increased ionic interaction strength. However, $\tau_s$ decreases slightly with increasing $p$ for low sulfonation degrees ($x < 80$), and overlaps for different $p$ when $x > 80$, where $\tau_s$ starts to show a rapid
increase with increasing $x$ (Figure 6.6c). Under the same Na content, the increase of free acid groups, i.e. increasing sulfonation degree, $p$, increases the segmental relaxation time $\tau_0$ (Figure 6.6b), but significantly decreases the ionic dissociation time $\tau_s$ (Figure 6.6d). It indicates that the free acid group may act as a polar plasticizer, weaken the ionic interaction between Na sulfonates, and accelerate the ionic dissociation. This plasticization effect was also observed in PEMA ionomers, where the viscosity of partially neutralized ionomers increased substantially if all the unneutralized acid group was converted into ethyl esters.  

In order to elucidate the mechanism of the plasticization effect, Figure 6.7 compares the LVE behavior of partially neutralized ionomers and blends of unneutralized and fully neutralized ionomer containing the same Na content. For the partially neutralized ionomer, both Na sulfonate groups and acid groups were randomly distributed among the different chains. It means every chain contains both Na sulfonates and acid groups. Whereas the polymer chain in the ionomer blends contains either Na sulfonates or acid groups. If the acid groups are associated with the Na sulfonates within the same ionic aggregate, the blend will show similar LVE behavior with partially neutralized ionomer. Otherwise, there might be a big difference in the LVE behavior because the ionomer containing only acid groups relaxes much faster than those containing both acids and salts. As shown in Figure 6.7, for all three different Na contents, the ionomer blends exhibit almost the same LVE behavior with that of partially neutralized ionomer. This is consistent with a previous study of partially PEAA ionomers where the partially neutralized PEAA ionomers showed similar melt indices, infrared spectra and mechanical properties with the blends of highly
neutralized and unneutralized PEAA ionomers.\textsuperscript{92} The consistent LVE behavior between partially neutralized ionomers and ionomer blends indicates that acid groups and metal salts are associated within the same aggregates. This result is in accordance with the morphological and dielectric study of SPS ionomers, in which it was found that the size of the ionic aggregates is independent of the neutralization degree but the ionic aggregates contain more metal sulfonates groups with increasing neutralization degree.\textsuperscript{34}

Figure 6.6 Effect of neutralization degree on the segment relaxation time $\tau_0$ and ionic dissociation time $\tau_s$ determined from the reversible gelation model. In panel c, the dashed lines show the predictions of Eq. 6.1, and solid line shows prediction from Eq. 6.5.
In particular, Figure 6.6c shows that the dissociation time $\tau_s$ is essentially controlled by the degree of neutralization. In our previous study on blends of fully neutralized SPS with two different alkali metal cations, we found that the ionic lifetime $\tau_{sb}$ of the blend is well related to $\tau_{s1}$ and $\tau_{s2}$ of two components as:

$$\frac{1}{\tau_{sb}} = \frac{\phi_1}{\tau_{s1}} + \frac{\phi_2}{\tau_{s2}}$$

(6.1)

Where $\phi_1$ and $\phi_2$ are the fraction of the cation 1 and 2 in the total cations, respectively. This equation means that the dissociation frequencies of different alkali sulfonates are additive. In other words, the dissociation frequency of one alkali sulfonate group is not strongly affected by the existence of a different kind of alkali sulfonate group. The validity of this mixing rule was tested here by regarding 1 and 2 as sodium sulfonate and sulfonic.
acid, respectively. The prediction of Eq 6.1 with \( \tau_{s1} \) and \( \tau_{s2} \) being chosen as \( \tau_s \) of fully neutralized and non-neutralized SPS (neutralization degree \( x = 100 \) and 0) is shown Figure 5c, which underestimates \( \tau_{sb} \) of the partly neutralized samples. The degree of this underestimation increases with the degree of neutralization initially and then decreases gradually until it disappears at \( x = 100 \). This result further prove our previous hypothesis that a strong interaction exists between sodium sulfonate and sulfonic acid groups.

Register and coworkers attributed the interaction to a plasticizing effect on the ionic groups from the acid groups.\(^6\),\(^1\)\(^0\) In our previous study on the dynamic change of an ion-containing polymer along the ionomer-to-polyelectrolyte transition upon addition of polar plasticizer, we found that the polar plasticizer imparts two major effects on the ionic aggregates, decreasing the \( T_g \) the localized ionic aggregates and the softening of the electrostatic interaction between ions.\(^1\)\(^1\)\(^9\) The viscosity reduces significantly when only small amount of the plasticizer is introduced, which is much stronger than that expected from the decrease of aggregate \( T_g \), and appears to be mainly controlled by the softening of the electrostatic interaction.

In this study, both effects of polar plasticization were observed from the values of Rouse relaxation time \( \tau_0 \) and the ionic dissociation time \( \tau_s \). Although the \( T_g \) of the polymer matrix remains constant for different neutralization degrees, the increase of neutralization degree \( x \) increases the segmental relaxation \( \tau_0 \) for all three ionomers, indicating the increase of aggregate \( T_g \) upon increasing \( x \). The softening of the ionic interaction upon increasing \( x \) can be clearly seen from the dramatic increase of the ionic dissociation time \( \tau_s \). Increasing
from 0 to 100 increases the $\tau_s$ by around 6 orders of magnitude, however, such increase of $x$ only enhances $\tau_0$ by several folds. The differences between $\tau_0$ and $\tau_s$ demonstrates the softening of the ionic interaction is responsible for the dramatic plasticization of the acid groups.

6.3.2 Steady shear behavior

Among all three ionomers, Na1.2-x ionomers have the lowest melt viscosity. Therefore, Na1.2-x ionomers were chosen as an example to investigate the effect of neutralization degree on the steady shear behavior. As shown in Figure 6.8, when $x \leq 76$, the steady state viscosity exhibits a Newtonian behavior at low shear rates followed by a shear thinning behavior at higher shear rates. When $x \geq 89$, an evident melt fracture, following the Newtonian region, was clearly observed. Those data points obtained after the occurrence of melt fracture were denoted as open symbols in Figure 6.8. The melt fracture has also been observed in the shear and extension flow of SPS ionomers with $p > p_c$, and it was attributed to the breakup of the brittle ionic network. As shown in Figure 6.1, the plateau in the storage modulus starts to occur when $x \geq 89$, indicating a formation of ionic network. Therefore, the catastrophic failure of the ionic network shall be responsible for the melt fracture in the partially neutralized ionomers.
Figure 6.8 Steady shear behavior of Na1.2-x ionomers at 180°C. Open symbols denote the appearance of melt fracture.

Figure 6.9 Effect of neutralization degree on the zero-shear viscosity of Na1.2-x ionomers at different temperatures.

For all Na1.2-x ionomers, the onset of the shear thinning or melt fracture was shifted
to lower shear rates with increasing $x$ because of the increased ionic interaction strength. Meantime, the zero-shear viscosity also increases with increasing $x$, as clearly seen in Figure 6.9. For all four temperatures investigated (170 to 200 °C), the zero-shear viscosity increases rather slowly when $x \leq 76$, but becomes rather rapidly when $x \geq 89$. This transition in the $x$ dependence of zero-shear viscosity is consistent with the trend observed in the ionic dissociation time (Figure 6.6c), both occurring at $x = 89$. The significant increase of the melt viscosity near the full neutralization further supports our previous speculation that the major effect of the acid groups is to soften the ionic interaction between Na sulfonates. Otherwise, if the plasticization effect is solely due to the decrease of aggregate $T_g$, a reasonable explanation for the rapid increase of melt viscosity at $x \sim 90$ is that the measurement temperature is very close to the $T_g$ of the ionic aggregate. Following this explanation, a natural expectation is to increase $T$ would lead to less abrupt increase of the viscosity with neutralization degree therein. In contrast to this expectation, it is evident in Figure 6.9 that increasing measurement $T$ from 170°C to 200°C does not lead to apparently weaker $T$ dependence of $\eta_0$ near the full neutralization, the $T$ dependences of $\eta_0$ are quite similar in a $T$ range between 170°C and 200°C. Therefore, we can conclude that the softening of the ionic interaction controls the abrupt increase of $\eta_0$ with degree of neutralization near the full neutralization.

6.3.3 Dielectric relaxation behavior

In order to figure out the softening mechanism of acid groups, the dielectric response spectroscopy measurements were conducted on the PS precursor, SPS ionomers with and
without neutralization. Figure 6.10a compares the frequency dependence of the dielectric loss $\varepsilon''$ for PS precursor and unneutralized Na$p$-0 ionomers with different $p$ at 140°C. Apparently, increasing the $p$ intensifies and delays the segmental $\alpha$ process due to the increase of the density of polar sulfonic acid groups. Figure 6.10b compares the dielectric loss $\varepsilon''$ against angular frequency $\omega$ for the Na2.7-$x$ ionomers with different neutralization degrees at 140°C. The dielectric process broadens significantly with neutralization, and finally separates into two processes at high degree of neutralization, $x \geq 50$.

A common trend can be clearly observed in Figure 6.10a and 6.10b is that the high frequency data shows an increase of amplitude with increasing amount of polar sulfonic acid groups. To quantitatively test this trend, the dielectric loss $\varepsilon''$ in Figure 6.10 is normalized by the fraction of monomers containing sulfonic acid groups: the raw $\varepsilon''$ data are divided by $y$ and plotted against $\omega$, with $y = 1.2\%$, $1.5\%$, and $2.7\%$ for unneutralized SPS, and $y = 2.7\% \times (1-x)$ for Na2.7-$x$ ionomers. The normalized data $\varepsilon''/y$ is plotted against $\omega$ in Figure 6.11, which exhibits similar amplitude at high frequency, suggesting that the dielectric intensity at $\omega > 10^5$rad/s is controlled by the density of polar acid groups. The only exception is the Na2.7-91 ionomer, which shows an amplitude well above all the other curves. This should be attributed to the large contribution of $\varepsilon''$ from the $\alpha$ segments of PS when the density of sulfonic acid group is so low ($= 2.7\% \times [1-91\%] = 0.24\%$) that the normalization based on density of polar acid groups becomes unsuitable. This point can be easily understood by taking a close look at Figure 6.10b, where the Na2.7-91 sample exhibits an intensity very close to that of PS at high $\omega$, indicating that the dielectric loss
therein is mainly contributed from the PS segments.

Figure 6.10 Comparison of dielectric loss $\varepsilon''$ against angular frequency $\omega$ at 140 °C for (a) PS and unneutralized SPS ionomers with degrees of sulfonation of 1.2mol%, 1.5mol%, and 2.7mol%. (b) Na2.7-x ionomers with the neutralization degree $x$ as indicated.

For partially neutralized Na2.7-x samples (Figure 6.10b), one additional dielectric process occurs at $\omega<10^5 \text{rad/s}$, which tends to be intensified and delayed with higher $x$. We speculate that this process is mainly contributed from a fluctuation of ionic groups within the aggregate. The delay of this dielectric process means that the polarity and the amount
of mobile ionic groups (acid groups) within the aggregate decreases with the increase of \( x \).

The comparisons in Figures 6.10 and 6.11 strongly suggest that the polar acid groups tend to enhance the polarity, thereby soften the ionic interaction between Na sulfonates. The disappearance of this softening effect near the full neutralization should be responsible for the abrupt increase of melt viscosity and ionic dissociation time therein (Figure 6.6c and Figure 6.9).

![Figure 6.11 Comparison of dielectric loss \( \varepsilon'' \) normalized by the fraction of monomers containing sulfonic acid groups, and plotted against angular frequency \( \omega \) for PS and sulfonated PS with degree of sulfonation of 1.2mol\%, 1.5mol\%, and 2.7mol\%, and Na2.7-\( x \) ionomers with the neutralization degree \( x \) as indicated.](image)

Figure 6.12 compares the intensities of dielectric \( \alpha \) relaxation, \( \Delta \varepsilon \), as functions of temperature \( T \) for PS precursor and Na\( p \)-0 ionomers with \( p = 1.2, 1.5, \text{ and } 2.7 \text{mol\%}. \)
Obviously, $\Delta \varepsilon$ increases with the increase of the density of the polar acid groups (increasing $\rho$). To quantify this effect, the dielectric intensity was analyzed by the Onsager equation:

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_s(\varepsilon_s + 2)^2} = \frac{\nu_{PS}m_{PS}^2}{9\varepsilon_0kT} + \frac{\nu_{SPS}m_{SPS}^2}{9\varepsilon_0kT}$$

(6.2)

Where $\varepsilon_s$ and $\varepsilon_\infty$ are dielectric constants before and after the $\alpha$ relaxation with $\varepsilon_\infty = \varepsilon_s + \Delta \varepsilon$, $\nu_{PS}$ and $\nu_{SPS}$ are number densities of PS and SPS monomeric segments, respectively, $m_{PS}$ and $m_{SPS}$ are dipole moments of the PS and SPS segments, respectively.

For PS precursor, only the first term remains on the right side of Eq 6.2. By taking $m_{PS}$ as a fitting parameter, the dielectric intensity $\Delta \varepsilon (= \varepsilon_s - \varepsilon_\infty)$ of PS precursor was fitted with the Eq 6.2, where $\varepsilon_\infty = 2.4$ and $\nu_{PS} = \rho N_{AV}/M_{0,PS}$, in which $N_{AV}$ is the Avogadro number, $\rho$ and $M_{0,PS}$ are the density and molecular weight per monomer of PS, respectively, with $\rho = 1.1g/cm^3$ and $M_{0,PS} = 104g/mol$. The dipole moment of the PS was then determined from the fitting as $m_{PS} = 0.095D$. The correspondingly fitted data was plotted as grey curve in Figure 6.12, which agrees well with the experimental results of PS (grey star symbols).

After inputting $m_{PS} = 0.095D$, $\nu_{PS} = (1-p\%)\rho N_{AV}/[p\%M_{0,SPS}+(1-p\%)M_{0,PS}]$ and $\nu_{SPS} = p\%\rho N_{AV}/[p\%M_{0,SPS}+(1-p\%)M_{0,PS}]$ (the molecular weight per monomer of SPS is $M_{0,SPS} = 184g/mol$) into Eq 6.2, $\Delta \varepsilon$ of the three NaP-0 ionomers (shown as square, circle and diamond symbols in Figure 6.12) were fitted by taking $m_{SPS}$ as the fitting parameter. The fitting results (curves) agree reasonably with the experimental results (symbols), yielding $m_{SPS} = 1.7D$. The agreement between the experimental data and the prediction of Eq 6.2
can also be seen in the inset graph of Figure 6.12, where Δε at $T_r = 140^\circ$C were plotted against the degree of sulfonation, $p$.

![Graph showing dielectric intensity $\Delta \varepsilon$ as a function of $1000/T$ for PS and Na$p$-0 ionomers with $p = 1.2$, 1.5, and 2.7 mol%. The curves are predictions of Eq 6.2 with two fitting parameters, i.e. dipole moments of PS and SPS monomeric segments as $m_{PS} = 0.095$D and $m_{SPS} = 1.7$D. Inset shows $\Delta \varepsilon$ against the degree of sulfonation $p$ at $T_r = 140^\circ$C, the curve is the prediction of Eq. 6.2.]

Figure 6.12 Comparison of dielectric intensity $\Delta \varepsilon$ of $\alpha$ relaxation as functions of $T$ for PS and Na$p$-0 ionomers with $p = 1.2$, 1.5, and 2.7 mol%. The curves are predictions of Eq 6.2 with two fitting parameters, i.e. dipole moments of PS and SPS monomeric segments as $m_{PS} = 0.095$D and $m_{SPS} = 1.7$D. Inset shows $\Delta \varepsilon$ against the degree of sulfonation $p$ at $T_r = 140^\circ$C, the curve is the prediction of Eq. 6.2.

As exhibited earlier in Figure 6.6c, the ionic dissociation time $\tau_s$ is essentially controlled by the degree of neutralization. In other words, $\tau_s$ mainly depends on the average fraction of the acid groups in the ionic aggregates. The dielectric results in Figures 6.10-6.12 suggest that the ionic dissociation might be controlled by the localized dielectric constant within the ionic aggregates. Therefore, the Onsager equation is utilized to
determine the localized dielectric constant within the ionic aggregates for different neutralization degrees. Based on the relation between the dielectric constant and the activation energy of the ionic interaction, the ionic relaxation time can be readily obtained.

In general, the activation energy of the ionic interaction is the Coulomb energy\(^{119}\)

\[
E_a = \frac{e^2}{4\pi\varepsilon_0\varepsilon r}
\]  

(6.3)

where \(e\) is the elementary charge, \(r\) is the radius of the ion, \(\varepsilon_0\) is the absolute dielectric permittivity, and \(\varepsilon_s\) is the dielectric constant of the surrounding medium. The ionic dissociation time \(\tau_s\) is related to the Rouse relaxation time \(\tau_0^{114}\)

\[
\tau_s = \tau_0 \exp \left( \frac{E_a}{kT} \right)
\]  

(6.4)

Thus the \(\tau_s\) of the partially neutralized ionomer with the neutralization degree of \(x\%\) can be obtained from Eq. 6.5:

\[
\tau_s(x\%) = \tau_0(x\%) \exp \left( \frac{E_s(x\%)}{kT} \right) = \tau_0(x\%) \exp \left( \frac{E_s(100\%)/\varepsilon_s(100\%)}{\varepsilon_s(x\%)kT} \right)
\]  

(6.5)

where \(E_s(100\%)\) is the activation energy of the fully neutralized ionomer \((x = 100)\), \(\varepsilon_s(x\%)\) is the localized dielectric constant within the aggregates. Specifically, based on the values of \(\tau_s\) and \(\tau_0\) (shown in Figure 6.6a and 6.6c), \(E_s(100\%)\) was determined to be 17.6, 17.5 and 16.1 \(kT\) for Na1.2-100, Na1.5-100, and Na2.7-100 ionomers, respectively. For simplicity, \(E_s(100\%)\) was fixed as 17.1 \(kT\), the average activation energy of three \(Nap\)-100 ionomers, and \(\tau_0(x\%)\) was fixed as 130 \(\mu s\), the average \(\tau_0\) for the six \(Nap-x\) ionomers with \(p=1.2, 1.5,\) and 2.7, and \(x = 0\) and 100. Meantime, the localized dielectric constant \(\varepsilon_s(x\%)\)
was determined from the Eq. 6.2 following the same procedure shown in Figure 6.12, where \( v_{SPS} = (1 - x\%) \rho N_{AV}/M_{0,SPS} \), \( m_{SPS} = 1.7D \), and the first term on the right side of Eq. 6.2 was kept as zero.

Remarkably, the Eq. 6.5, though quite simple, predicts well the plots of \( \tau_s \) against the neutralization degree shown in Figure 6.6c. The excellent agreement between experimental data and the model further proves that the acid groups increase the localized dielectric constant within the ionic aggregates, thus soften the ionic interaction of Na sulfonates and accelerate the ionic dissociation.

6.4 Conclusions

In this study, the LVE behavior of SPS ionomers with different degrees of neutralization was investigated and compared with the predictions from the reversible gelation model. It was found that the dissociation time of the ionic groups within partly neutralized SPS ionomers is essentially determined by the degree of neutralization, \( x \). Increasing \( x \) significantly enhances the ionic dissociation time and zero shear viscosity, especially close to the full neutralization. The strong increase of viscosity near the complete neutralization is unlikely to be governed solely by the reduced \( T_g \) of the ionic aggregates, but more likely to be related to the increased strength of ionic interaction due to the decrease of the density of the polar sulfonic acid groups within the aggregates.

Therefore, it is quite possible that the acid groups and metal sulfonate groups are all condensed in the ionic aggregates to serve as crosslinks. There are two main interactions between them: (1) the acid groups plasticized the aggregate region where the ionic groups
locate, and (2) the acid groups, as a polar medium in the aggregates, soften the electrostatic interaction between metal sulfonate groups, where the latter is responsible for the dramatic plasticization effect of the unneutralized acid groups.

The dielectric relaxation behavior of the SPS ionomers with and without neutralization also proves the above argument. The polar acid groups control the amplitude of $\alpha$ relaxation when the density is sufficient, but lose this control when the $x \geq 90\%$, where $\eta_0$ increases significantly with neutralization degree. With the help of Onsager equation, the localized dielectric constant within the ionic aggregates was determined for ionomers with different $x$, then used to predict the ionic dissociation time based on the relation between the dielectric constant and the activation energy of the ionic interaction. The excellent agreement between the model predictions and experimental data demonstrates that the major effect of sulfonic acid groups is to soften the ionic interaction between metal sulfonate, thereby accelerating the ionic dissociation.
CHAPTER VII

RHEOLOGY OF OLIGOMERIC SULFONATED POLYSTYRENE IONOMERS
NEUTRALIZED WITH DIVALENT METAL CATION

7.1 Introduction

Copolymers containing small amount (typically less than 15 mol\%) of ionic monomers, termed ionomers, have been widely used in the industry as polymer blends compatibilizers,\textsuperscript{147} packaging films,\textsuperscript{1} and self-healing materials etc.\textsuperscript{145} Those applications take advantage of their excellent physical, mechanical and rheological properties provided by the strong dipolar or ionic interaction between polar ionic groups.

The dynamics of ionomers strongly depends on the ionic interaction strength of the ion pairs. Sulfonated ionomers often possess a melt viscosity orders of magnitude higher than that of carboxylated ionomers.\textsuperscript{20} The rheological properties of both sulfonated and carboxylated ionomers will change dramatically if the sulfonic/carboxyl acid groups are neutralized into different metal salts. The effect of alkali cations on the rheological behavior of ionomers has been investigated extensively,\textsuperscript{32, 90} and it was found that both terminal relaxation time and melt viscosity increased with increasing Coulomb energy of the ion pair, $cq/a$, where $c$ is the concentration of ionic groups, $q$ and $a$ are charge and radius of metal cation, respectively.\textsuperscript{32} However, only limited studies have been performed
so far to the understanding of the effect of divalent cation, especially divalent transition metal cation, on the rheology of ionomers. For instance, it was found that barium (Ba$^{2+}$) and magnesium (Mg$^{2+}$) neutralized sulfonated EPDM ionomer (SEPDM) melts exhibited a rather prolonged rubbery plateau than that of Zn or Pb neutralized SEPDM. In the concentrated SEPDM solution of paraffinic oil, the terminal relaxation time of divalent metal salts shows the order of $\tau_{\text{Ba}} > \tau_{\text{Mg}} > \tau_{\text{Zn}}$, while the cation radius is $r_{\text{Ba}} > r_{\text{Zn}} > r_{\text{Mg}}$. This phenomenon clearly violates the rule observed in the alkali metal cation that a stronger ionic interaction is favored by a smaller cation radius. Similarly, in the study of telechelic carboxylated polybutadiene (CPBD) ionomers, the viscosity of the ionomer melt follows the order of $\eta_{\text{Ba}} > \eta_{\text{Mg}} > \eta_{\text{Ca}} > \eta_{\text{Zn}}$, though the order of cation radius is $r_{\text{Ba}} > r_{\text{Ca}} > r_{\text{Zn}} > r_{\text{Mg}}$. In addition, numerous studies have demonstrated that Zn neutralized ionomer has relatively lower melt viscosity than other metal cations despite its relatively small cation radius.

Compared to alkali cations, the alkaline earth and divalent transition metal cations show a rather complex effect on the viscosity of sulfonated or carboxylated ionomers. Up to now, no theory does a perfect job at describing their complex effect on the rheological behavior. One possible reason is that it is quite difficult to complete neutralize the acid groups into divalent metal salts. A small amount of unneutralized acid group could decrease the viscosity by orders of magnitude. However, if excess neutralizing agent was used, the divalent cation may be connect with only one acid group, and the remaining anion, such as hydroxyl ion (OH$^{-}$) and acetate ion (Ac$^{-}$), could serve as a plasticizer. Both under- and over-

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neutralization might complex the effect of divalent metal cations on the rheological behavior. Another explanation for the complexity of transition metal cation is that transition metal might form covalent bonds with the acid groups, which is different from the ionic bonds formed in the alkali/alkaline earth metal salts. In addition, most of studies discussed above were based on entangled ionomers. The use of high molecular weight ionomers has a serious drawback that the effect of the ionic interactions on the rheological behavior is often complicated or even hidden by the chain entanglements.

Therefore, oligomeric sulfonated polystyrene (SPS) has recently been adopted as a model ionomer to investigate the effect of ionic content, metal cation, neutralization degree on the shear and extensional rheology of random ionomers. Both neat ionomers and the blends of two ionomers experience a sol-gel transition at a gel point, where the ionomer system contains one ionic group per chain on average. Close to the gel point, ionomers show two characteristic power law relaxations in the LVE behavior, which corresponds to the mean-field and critical percolation behavior. The effect of metal cation on the LVE behavior was found to be highly dependent on the ionic concentration. Below the gel point, changing metal cation has little effect on the dynamic moduli of the ionomers. However, when the ionomer is close to or above the gel point, the type of alkali metal cations significantly affects the terminal relaxation behavior. A fast terminal relaxation is favored by the smaller cation radius, which corresponds to a weaker Coulomb energy for alkali cations. Based on the mean field theory of Rubinstein
and Semonov\textsuperscript{136,137}, a reversible gelation model was proposed recently to predict the LVE behavior of random ionomers. With only two parameters, the Rouse relaxation time of the Kuhn segment $\tau_0$ and the ionic dissociation time $\tau_s$, a good agreement was achieved between the experimental data and the model predictions for both neat ionomers and ionomer blends. The effect of the alkali cation was successfully quantified by the ionic dissociation time $\tau_s$. In particular, the reciprocal of the ionic dissociation time for the blends of different alkali cations was found to be the linear addition of the reciprocal of $\tau_s$ for two component alkali cations.\textsuperscript{160}

In this chapter, SPS ionomers with a molecular weight of $M_w = 13.5$ k g/mol, and degrees of sulfonation below, close to, and above the gel point were neutralized by divalent metal cations, including alkaline earth and transition metal cations. The effect of divalent metal cation on the LVE behavior was investigated and compared with predictions from the reversible gelation model. The obtained ionic dissociation times were discussed with respect to the radius and electron configuration of the divalent cations. Details are described below.

7.2 Experimental section

This section described the synthesis and the characterization of the rheological behavior of SPS ionomers with different divalent metal cations.

7.2.1 Materials

Oligomeric polystyrene (PS13.5) with molecular weight $M_w = 13.5$ k g/mol and narrow polydispersity, PDI $< 1.06$, was provided by Pressure Chemical Co. (Pittsburgh,
PA). The sulfonation of the PS was conducted in a ~10wt% 1,2-dichloroethane (DCE) solution using a sulfonation agent, acetyl sulfate\textsuperscript{14}, which was freshly prepared through the reaction of concentrated sulfuric acid with 60 mol% excess of acetic anhydride in DCE at 0°C. After adding acetyl sulfate into the PS/DCE solution (~200ml) at ~50°C under constant stirring, the mixture was allowed to react for 1h, afterwards the reaction was terminated by adding ~2ml of 2-propanol. It should be mentioned that the substitution of hydrogen to sulfonic acid group is an electrophilic substitution, and it occurs mainly at the para-position of the phenyl ring.\textsuperscript{157} The sulfonated polystyrene (SPS13.5) was collected after precipitating the mixture in boiling de-ionized water, washing the precipitate three times with di-ionized water, drying the powder in air at 70°C for 1 day, and finally at 120°C in vacuum oven for 1 week. The degree of sulfonation was measured through the sulfur elemental analysis by Robertson Microlit Analysis (Madison, NJ).

Three SPS13.5 samples were prepared with ionic concentration of 0.20, 0.76 and 1.5 mol%, which corresponds to 0.3, 1 and 2 ionic groups per chain on average. Note that the sulfonation reaction is a random process, and it will produce a bimodal distribution of the SPS chains with different ionic groups.\textsuperscript{142} Fully neutralized divalent metal salts of SPS13.5 were prepared by adding a predetermined amount of metal acetate, which was previously dissolved in a small amount of methanol or water, into a 15wt% solution of SPS acid derivative in a 90/10 (v/v) mixture of toluene and methanol. After stirring the solution for 30min, the neutralized SPS13.5 salts were recovered following the procedures as described above for SPS acid derivatives. Specifically, SPS13.5 acid derivative was neutralized by
different amount of zinc acetate, ranging from the stoichiometric ratio to far above, in order to find the optimum amount of neutralizing agent to achieve the complete conversion of acid groups into divalent metal salts. Afterwards, this optimum amount was used for the preparation of all other divalent metal salts. The neutralization of SPS13.5 ionomers into Na and Cs salts follows the same procedure for divalent metal cations except that a 50mol% excess of neutralizing agent was used. The sample nomenclature used herein is MSPS13.5-\(p\), where M represents the metal cation (\(\text{Na}^+, \text{Cs}^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}\)) and \(p\) represents the ionic content in mol% \((p = 0.20, 0.76, \text{and} \ 1.5)\).

7.2.2 Materials characterization

Small amplitude oscillatory shear experiments were conducted in a TA Instruments ARES-G2 rheometer using either 25 or 8mm parallel plates. Dynamic frequency sweeps were performed at a temperature range of 110-250°C, a frequency range of 0.16-250 rad/s, and a strain amplitude within the linear viscoelastic regime. Considering the glass transition temperature of SPS13.5 ionomers varies by less than 5 °C, time-temperature-superposition (TTS) master curves were constructed using the same reference temperature \(T_r = 140 \ °C\).

Small angle X-ray scattering (SAXS) measurements were performed in a Rigaku MicroMax-002+ microfocus sealed tube, where X-ray source was produced from Cu Kα radiation with a wavelength of 1.54 Å, a divergence of 4.8 mrad and a focal spot of 20 × 20 μm. The scattering data was collected over a scattering vector \(q\) of 0.01-0.17 Å\(^{-1}\) and a time period of 10 min for each sample.
7.3 Results and discussion

This section investigated the effect of divalent metal on the linear rheological behavior of SPS ionomers.

7.3.1 Effect of neutralizing agent

One of the main difficulties in the research of divalent cation neutralized ionomers is that the complete neutralization, i.e. the complete conversion of the acid groups to metal salts, is hard to achieve or determine. If less neutralizing agent was added, the remaining unneutralized acid group could significantly promote the terminal relaxation of ionomers.\(^{100}\) However, if excess neutralizing agent was used, the divalent cation may only be connected by one ionic group. For instance if ZnAc\(_2\) was used to neutralize sulfonic acid group, an excess of ZnAc\(_2\) may lead to the formation of mono-sulfonate SO\(_3^-\)Zn\(^{2+}\)Ac\(^-\), which might promote the relaxation in the similar manner that unneutralized acid groups do.\(^{159}\)

Figure 7.1 shows the effect of ZnAc\(_2\) content on the master curves of storage modulus, \(G'\), and loss modulus, \(G''\), at \(T_r = 140^\circ\text{C}\) for ZnSPS13.5-1.5 ionomers, where a ratio of 100% means a stoichiometric amount of ZnAc\(_2\) was used as neutralizing agent. It should be mentioned that all ZnSPS ionomers were carefully washed three times with boiling di-ionized water in order to remove any possible residue of ZnAc\(_2\). When 100% ZnAc\(_2\) was used, the ionomer shows a very short plateau in the storage modulus, and the transition to the terminal relaxation occurs at \(~0.1\) rad/s. The increase of ZnAc\(_2\) amount to 115% delays the onset frequency of the terminal relaxation to one order of magnitude lower, indicating
the increase of terminal relaxation time upon the addition of extra ZnAc₂. Further decreasing the ZnAc₂ amount slightly delays the terminal relaxation until it reaches 160%. Afterwards, the terminal relaxation time decreases with the increasing ZnAc₂ amount due to the conversion of di-sulfonate group SO₃⁻Zn²⁺SO₃⁻ to less strongly associating mono-sulfonate group SO₃⁻Zn²⁺Ac⁻.

The terminal relaxation time and zero-shear viscosity were calculated from the terminal tails of $G'$ $\propto \omega^2$ and $G''$ $\propto \omega^1$ in the master curves using Eq. 7.1

$$\tau = \lim_{\omega \to 0} \left[ \frac{G'(\omega)}{\omega G''(\omega)} \right] \quad \eta = \lim_{\omega \to 0} \left[ \frac{G''(\omega)}{\omega} \right]$$

(7.1)

The obtained values were plotted against the ZnAc₂ amount and shown in Figure 7.1c. Both $\tau$ and $\eta$ show similar trend with respect to the ZnAc₂ amount, indicating the independence of shear compliance ($J = \tau / \eta$) on the neutralization degree, which is consistent with previous study of partially neutralized PEMA ionomers. The increase of ZnAc₂ amount from 100% to 160% increases $\tau$ and $\eta$ by nearly 2 orders of magnitude. It demonstrates that adding a stoichiometric amount of ZnAc₂ cannot convert all the acid groups into metal sulfonates because of the reaction efficiency of the neutralization. When the ZnAc₂ amount is above 160%, $\tau$ and $\eta$ decrease slightly with the increasing ZnAc₂ amount. It means that the Ac⁻ in the mono-sulfonate group SO₃⁻Zn²⁺Ac⁻ exhibit much weaker plasticization effect than that of unneutralized acid groups. It is clearly shown that both $\tau$ and $\eta$ reach the maximum when 160% of ZnAc₂ was added, which corresponds that almost all acid groups were converted into di-sulfonate groups. One
may argue that the system might contain a small amount of ZnAc$_2$, which will also affect the terminal relaxation behavior. Makowski et al. found that excess ZnAc$_2$ acted as an ionic plasticizer and decreased the melt viscosity of SEPDM ionomers.\textsuperscript{87} Similarly, in SPS system, the presence of excess ZnAc$_2$ will probably promote the terminal relaxation as a plasticizer rather than a reinforcer. Thus there shall not be excess ZnAc$_2$ in the ionomer added with 160\% of ZnAc$_2$, otherwise, the maximum $\tau$ would be reached at lower ZnAc$_2$ amount.
Figure 7.1 Storage moduli $G'$ (a) and loss moduli $G''$ (b) master curves at $T_r = 140$ °C for ZnSPS1.5 ionomers neutralized with different amount of ZnAc2, and (c) effect of ZnAc2 amount on the terminal relaxation time and viscosity of ZnSPS1.5 ionomers.

In order to verify the rheological result, SAXS was utilized to study the microstructure of the ZnSPS13.5-1.5 ionomers neutralized with different amount of ZnAc2. As shown in...
Figure 7.2, all four samples show similar scattering intensity at high $q$, where the ionic peak typically occurs. However no ionic peak was observed in this $q$ region due to the relatively low sulfonation level. In particular, the 100% sample show a rather higher scattering upturn in the low $q$ region than other samples. Register et al. investigated the effect of the neutralization degree on SAXS behavior of the Nickle neutralized SPS, found that the upturn scattering intensity decreases with the neutralization degree.\textsuperscript{31} Considering the fast terminal relaxation of the 100% sample (Figure 7.1), the high upturn scattering intensity should be ascribed to the presence of the unneutralized acid groups. The other three samples, however, show similar scattering upturn behavior at low $q$. This indicates all three ionomers were almost fully neutralized, which is consistent with the LVE behavior shown in Figure 7.1. Based on the LVE and SAXS results, all divalent metal neutralized SPS13.5 ionomers discussed in the next sections were neutralized with 160% of metal acetate in order to achieve the complete neutralization.
7.3.2 Alkaline earth metals

The gel point for the SPS13.5 ionomers was determined to \( p_c = 100\text{mol}\%/(N-1) \)
\( = 0.78 \text{ mol\%}. \)\textsuperscript{154} Below the gel point (\( p < p_c \)), the ionomer behaves like a sol. Close to the
gel point, an ionic network (gel) starts to form, but the fraction of the gel is infinitely small.
Above the gel point (\( p > p_c \)), the system contain mixture of sol and gel, and the fraction of
gel increases with \( p \) until a complete gel is formed at \( p = 2p_c. \)\textsuperscript{154} In this contribution,
SPS13.5 ionomers with degrees of sulfonation below (\( p = 0.20 \text{ mol}\% \), close to (\( p = 0.76 \text{ mol}\% \)), and above (\( p_c < p = 1.5 \text{ mol}\% < 2p_c \)) the gel point were investigated with respect
to different divalent metal cations.

Figure 7.3 shows the LVE master curves and the model predictions for SPS13.5-\( p \)
ionomers neutralized with alkaline earth metal cations. Na and Cs salts of SPS13.5 ionomer
were also included for comparison. When $p < p_c$ (Figure 7.3a), TTS works quite well for all cations, and a plateau in storage modulus was not observed for both divalent and monovalent metal salts. Alkaline earth metal salts show similar dynamic modulus with that of Na and Cs salts, which is consistent with the model prediction that the LVE behavior of ionomer below the gel point is independent of the metal cations. The reversible gelation model fits $G'$ and $G''$ quite well except a weak underestimation of $G'$ in the terminal region. This discrepancy exists in both alkali and alkaline earth metal salts, and it was attributed to the neglect of the non-effective breakup of the ionic clusters in the model.

When $p \sim p_c$ (Figure 7.3b), similar to the alkali metal salts, the alkaline metal salts also show distinct power law relaxations in the LVE master curves: mean-field behavior ($G' \sim G'' \sim \omega^1$) at higher frequencies, critical percolation behavior ($G' \sim G'' \sim \omega^{2/3}$) at intermediate frequencies, and terminal relaxation behavior ($G' \sim \omega^2$, $G'' \sim \omega^1$). The model predicts $G'$ and $G''$ quite well for all metal salts, indicating the universality and validity of the reversible gelation model. TTS fails in the terminal region of $G'$ due to the overlap of two relaxation processes with different temperature dependence: the ionic dissociation and the Rouse relaxation the chain segment. Compared to Na salt, the Ba salt shows a much delayed terminal relaxation, while Sr, Ca, and Mg salts exhibit only slightly delay of the terminal relaxation.

For $p > p_c$ (Figure 7.3c), a plateau in $G'$ occurs with plateau modulus, $G_N$, independent of the monovalent and divalent metal cation. TTS fails in the valley of the $G''$ due to the overlap of Rouse relaxation and ionic dissociation. The model predicts well the
terminal relaxation of $G'$ but gives a higher $G_N$ because the model assumes that all strands (i.e., the chain between sulfonate groups) hold stress.\textsuperscript{154,160} Alkaline earth metal salts show a longer terminal relaxation time than that of Na salt, and their relaxation times follow the order of $\tau_{\text{Ba}} > \tau_{\text{Sr}} > \tau_{\text{Ca}} > \tau_{\text{Mg}}$. In other words, the Ba sulfonate groups have the strongest ionic interaction despite its largest cation radius in the alkaline earth metal. This order is in accordance with the previous study of SEPDM by Agarwal et al.\textsuperscript{65}, but violates the relation of $cq/a$ observed in alkali metal cations. This indicates that the Coulomb energy alone is not sufficient to describe the complex ionic interaction between divalent metal sulfonates, especially when the divalent cation is connected with two sulfonate groups.

Table 7.1 summarizes the Rouse relaxation time of an Kuhn segment ($\tau_0$) and the ionic dissociation time ($\tau_s$) obtained from the model fitting shown in Figure 7.1. $\tau_0$ increases with the sulfonation degree $p$ because of the restricted chain mobility. The type of cation has little effect on the Rouse relaxation time $\tau_0$, but significantly affects the value of ionic dissociation time $\tau_s$. A clear trend can be observed that the alkaline earth metals show stronger ionic interaction than that of Na and Cs, which is consistent with the previous study of SEPDM ionomers\textsuperscript{65} and a recent simulation result of SPS ionomers.\textsuperscript{98} For all alkaline earth metal cations, a larger $\tau_s$ is favored by a larger cation radius, which contradicts the trend observed in alkali cations.\textsuperscript{154,160} For alkali metal cation, one cation is only associated with one sulfonate group, the ion hopping process occurs when only one ionic group dissociates from the ionic aggregates, thus the ionic dissociation time is mainly related to the Coulomb energy of the ion pair. However, for alkaline metal cations, one
cation is associated with two sulfonate groups, the ion-hopping process requires both ionic
groups dissociate from the ionic aggregates at the same. In this case, the mobility of the
cation, i.e. the size of the cation, becomes dominating factor of the kinetics of ion-hopping.
A larger cation means a weaker mobility, and a higher activation energy, and thus a higher
dissociation time. Therefore, the ionic dissociation time, $\tau_s$, increases with the radius of the
alkaline earth metal cations.

Table 7.1 Rouse relaxation time ($\tau_0$) and ionic dissociation time ($\tau_s$) for MSPS13.5-0.20,
MSPS13.5-0.76, and MSPS13.5-1.5 ionomers (M = Na, Cs, Mg, Ca, Sr, Ba) at a
reference temperature of 140°C

<table>
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<tr>
<th></th>
<th>Na</th>
<th>Cs</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
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<td>29</td>
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<td>31</td>
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Figure 7.3 Storage moduli $G'$ and loss moduli $G''$ master curves at $T_r = 140 \, ^\circ C$ for (a) MSPS13.5-0.20, (b) MSPS13.5-0.76, and (c) MSPS13.5-1.5 ionomers (M = Na, Cs, Mg, Ca, Sr, Ba). The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior, and (III) terminal behavior. The solid lines are predictions from the reversible gelation model.
The shift factors used for master curves of MSPS13.5 ionomers shown in Figure 7.3 were plotted against the temperature in Figure 7.4, and their corresponding Williams-Landel-Ferry (WLF) constants were listed in Table 7.2. For all metal cations, the shift factors show a stronger temperature dependence with higher $p$. And the WLF constants, $C_1$ and $C_2$, increase with increasing $p$. The free volume theory predicts $C_1 \propto 1/f_r$ and $C_2 \propto f_r/\alpha_f$ with $f_r$ as the fractional free volume at $T_r$ and $\alpha_f$ as the free volume expansion coefficient. The increase of $C_1$ and $C_2$ indicates that the fractional free volume $f_r$ and the volume expansion coefficient $\alpha_f$ decreases with the increasing $p$. This phenomenon has been widely observed in previous studies, and it was attributed to the densification of polymer chains. When $p = 0.20$, the alkaline earth metal salts show similar shift factor with that of Na and Cs salts, but have a slightly higher shift factor at high temperatures, which indicates that the ionic dissociation of alkaline earth metal salts have a weaker temperature dependence. This difference in the temperature dependence of alkali and alkaline earth metal salts becomes rather significant when $p = 0.76$ and 1.5. Specifically, when $p = 1.5 > p_c$, the alkaline earth metal salts show much higher shift factors than Na salt after $T > 150$ °C. At higher temperature the shift factors of alkaline earth metal salts follow an order of $a_T(Ba) > a_T(Sr) > a_T(Ca) > a_T(Mg)$, which is consistent with the trend observed in the ionic dissociation time shown in Table 7.1. Correspondingly, both $C_1$ and $C_2$ decrease slightly with the increase of cation radius for alkaline earth metal cations, indicating that a bulky structure is formed for larger cations. These changes in the WLF constants further prove our previous hypothesis that the larger cation radius may restrict
the motion of the ionic groups and lead to the delayed ionic dissociation.

Table 7.2 WLF Constants for MSPS13.5-0.20, MSPS13.5-0.76, and MSPS13.5-1.5 ionomers (M = Na, Cs, Mg, Ca, Sr, Ba).

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<td>7.2</td>
<td>7.1</td>
<td>7.0</td>
<td>6.9</td>
</tr>
<tr>
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<td>95.8</td>
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<td>7.7</td>
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Figure 7.4 Time-temperature shift factor $a_T$ with respect to $T-T_r$ for (a) MSPS13.5-0.20, (b) MSPS13.5-0.76, and (c) MSPS13.5-1.5 ionomers ($M = \text{Na, Cs, Mg, Ca, Sr, Ba}$). The solid lines show the WLF fit.
7.3.3 Transition metals

In order to investigate the effect of transition metal cations on the LVE behavior of ionomers, four metals, Mn, Co, Ni, Zn, were chosen from the same period 4 but different groups in the periodic table. The latter three cations, Co²⁺, Ni²⁺, and Zn²⁺, have almost the same radius of 0.073nm and the Mn²⁺ has a smaller radius of 0.046nm. Figure 7.5 shows the comparison of the LVE behavior for SPS13.5 ionomers neutralized with transition metal and alkali cations. Similar to the alkali and alkaline earth metal salts, the transition metal salts behave as sol when \( p = 0.20 < p_c \), show characteristic power relaxation behavior when \( p = 0.76 \sim p_c \), and exhibit a plateau in storage modulus when \( p = 1.5 > p_c \). TTS fails in the terminal region of \( G' \) for \( p \sim p_c \) and before the peak of \( G'' \) for \( p > p_c \) due to the overlap of ionic dissociation and Rouse relaxation as discussed above. The reversible gelation model predicts reasonably well the dynamic moduli of all ionomers, but under-predicts the \( G' \) in the terminal region for \( p \sim p_c \), and over-predicts the plateau modulus \( G_N \) for \( p > p_c \), which is consistent with our previous observations in alkali and alkaline earth metal salts.\(^{154, 160}\) In accordance to the model predictions, changing cation do not significantly affect the dynamic moduli of ionomers with \( p < p_c \), but significantly alter their terminal relaxation time when \( p \sim p_c \) and \( p > p_c \). For both sulfonation levels \( (p = 0.76 \text{ and } 1.5) \), the terminal relaxation time follows the order of \( \tau_{\text{Ni}} > \tau_{\text{Na}} > \tau_{\text{Mn}} > \tau_{\text{Co}} > \tau_{\text{Zn}} > \tau_{\text{Cs}} \), and this difference in terminal relaxation becomes more evident for ionomers with higher \( p \) due to the enhanced ionic interaction.
Figure 7.5 Storage moduli $G'$ and loss moduli $G''$ master curves at $T_r = 140$ °C for (a) MSPS13.5-0.20, (b) MSPS13.5-0.76, and (c) MSPS13.5-1.5 ionomers (M = Na, Cs, Mn, Co, Ni, Zn). The colored regions correspond to: (I) mean field percolation behavior, (II) critical percolation behavior, and (III) terminal behavior. The solid lines are the model predictions.
The values of Rouse relaxation time ($\tau_0$) and ionic dissociation time ($\tau_s$) determined from the model fitting (shown in Figure 7.1) were summarized in Table 7.3. $\tau_0$ is independent of the cation type but increases with the sulfonation degree $p$ because the short time segmental relaxation is strongly related to the concentration rather than the type of ionic groups. The ionic dissociation time $\tau_s$ changes slightly for different $p$ but varies significantly for different transition metal cations. Unlike that of alkaline earth metal cations, three of the transition metal salts, i.e. Mn, Co, and Zn salts, show weaker ionic interaction strength, i.e. shorter $\tau_s$, than that of Na salt, while Ni salt shows a stronger ionic interaction. The order of $\tau_s$ is $\tau_s$(Ni) > $\tau_s$(Mn) > $\tau_s$(Co) > $\tau_s$(Zn) for the four divalent transition metals. Considering that Ni, Co, Zn cations have the same cation radius, the order of $\tau_s$ indicate that the ionic interaction strength of the transition metal cations is independent of the cation radius. Similar phenomenon has also been observed in other studies of transition metal salts of random ionomers\textsuperscript{65, 87, 192} and telechelic ionomers\textsuperscript{94, 96, 193}.

Different theories have been proposed to explain the difference in the rheology of ionomers neutralized by alkaline earth and divalent transition metal. Wilkes et al.\textsuperscript{101} suggested that the alkaline metal cations form ionic bonds with sulfonate groups, while the transition metal cations form covalent bonds due to the presence of electron in the $d$ orbital. Wilkes’ theory drives us to consider the different electron configuration of the transition metal cations. The electron configuration of Zn$^{2+}$ is [Ar]$3d^{10}$, Ni$^{2+}$ is [Ar]$3d^{8}$, Mn$^{2+}$ is [Ar]$3d^{5}$, and Co$^{2+}$ is [Ar]$3d^{7}$. According to the Hund’s rule, a given atom with the outmost subshell ($d$ orbital in this case) fully filled has the lowest energy. Zn$^{2+}$ has a filled $d$ orbital,
and thus the lowest energy. Therefore, the strength of the covalent bond between the Zn$^{2+}$ and SO$_3^-$ is the weakest among all four transition metal sulfonates. In particular, Ni$^{2+}$ has a configuration of [Ar]3$d^8$, the interaction with two SO$_3^-$ groups could offer Ni$^{2+}$ cation another two electrons to change the high energy 3$d^8$ to low energy 3$d^{10}$. It means that the SO$_3^-$Ni$^{2+}$SO$_3^-$ di-sulfonate groups form the most stable structure because more energy is needed to break up these covalent bonds. As a result, the Ni salt has the strongest ionic interaction strength among these four transition metal salts. This hypothesis also explains the similar ionic interaction strength of Mn$^{2+}$ and Co$^{2+}$ salts where the electron configuration of $d$ orbital is only partially filled before and after the formation of covalent bond with SO$_3^-$ groups.
Figure 7.6 Time-temperature shift factor $a_T$ with respect to $T-T_r$ for (a) MSPS13.5-0.20, (b) MSPS13.5-0.76, and (c) MSPS13.5-1.5 ionomers ($M = \text{Na, Cs, Mn, Co, Ni, Zn}$). The solid lines show the WLF fit.
Table 7.3 Rouse relaxation time ($\tau_0$) and ionic dissociation time ($\tau_s$) for MSPS13.5-0.20, MSPS13.5-0.76, and MSPS13.5-1.5 ionomers ($M = \text{Na, Cs, Mn, Co, Ni, Zn}$) at a reference temperature of 140°C

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Cs</th>
<th>Mn</th>
<th>Co</th>
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<td>34</td>
<td>27</td>
<td>27</td>
<td>27</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>$\tau_s$ (s)</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<tr>
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<td>36</td>
<td>35</td>
<td>36</td>
<td>35</td>
</tr>
<tr>
<td>$\tau_s$ (s)</td>
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<td>630</td>
<td>19000</td>
<td>32</td>
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<td></td>
</tr>
<tr>
<td>$\tau_0$ (μs)</td>
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<td>93</td>
<td>89</td>
<td>90</td>
<td>83</td>
</tr>
<tr>
<td>$\tau_s$ (s)</td>
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<td>18</td>
<td>1700</td>
<td>1180</td>
<td>11000</td>
<td>240</td>
</tr>
</tbody>
</table>

Figure 7.6 shows the temperature dependence of the shift factors for MSPS13.5 ionomers neutralized with divalent transition metals, and their corresponding constants determined from the WLF fitting were shown in Table 7.4. Similar with alkaline earth metal salts, the shift factors of transition metal salts exhibit a stronger temperature dependence for ionomers with higher $\rho$, and the effect of cation type on the shift factor becomes stronger at higher temperatures and higher $\rho$. $C_1$ and $C_2$ increase greatly with increasing $\rho$ but only varies slightly for different metal cations. The transition cation with the highest $\tau_s$ shows the highest shift factors at higher temperatures, which is consistent with the trend observed
in alkaline earth metal salts. At high temperatures the shift factor follow the same order of \( \tau \) as \( \alpha_T(\text{Ni}) > \alpha_T(\text{Mn}) > \alpha_T(\text{Co}) > \alpha_T(\text{Zn}) \), and the corresponding WLF constants, \( C_1 \) and \( C_2 \), decrease in the same sequence. The weaker temperature dependence of the shift factors may be correlated with a stronger covalent bonds between the metal cation and acid groups, with both related to the electron configuration of the transition metal cations.

Table 7.4 WLF Constants for MSPS13.5-0.20, MSPS13.5-0.76, and MSPS13.5-1.5 ionomers (M = Na, Cs, Mn, Co, Ni, Zn).

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Cs</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
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<tr>
<td>SPS13.5-0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_1 )</td>
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<td>7.2</td>
<td>7.0</td>
<td>7.0</td>
<td>6.9</td>
<td>6.9</td>
</tr>
<tr>
<td>( C_2(K) )</td>
<td>99.9</td>
<td>101.2</td>
<td>97.7</td>
<td>97.7</td>
<td>96.8</td>
<td>97.1</td>
</tr>
<tr>
<td>SPS13.5-0.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_1 )</td>
<td>7.8</td>
<td>8.2</td>
<td>7.1</td>
<td>7.5</td>
<td>6.9</td>
<td>8.0</td>
</tr>
<tr>
<td>( C_2(K) )</td>
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<td>105.9</td>
<td>96.2</td>
<td>102.8</td>
<td>94.7</td>
<td>103.8</td>
</tr>
<tr>
<td>SPS13.5-1.5</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>( C_1 )</td>
<td>9.3</td>
<td>10.1</td>
<td>8.1</td>
<td>8.8</td>
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<td>8.7</td>
</tr>
<tr>
<td>( C_2(K) )</td>
<td>113.9</td>
<td>122.8</td>
<td>103.0</td>
<td>110.0</td>
<td>99.8</td>
<td>111.5</td>
</tr>
</tbody>
</table>

7.4 Conclusions

In this contribution, we have examined the LVE behavior of oligomeric SPS ionomers neutralized to alkaline earth and divalent transition metal salts. A complete neutralization
of ionomers was achieved through adding 160% of the stoichiometric amount of neutralizing agents. Ionomers neutralized with divalent metals show similar dynamic response with those neutralized with alkalis: exhibiting a sol-like relaxation when $p < p_c$, showing characteristic power law relaxation behavior when $p \sim p_c$, and displaying a plateau in the storage modulus with the plateau modulus independent of cation type when $p > p_c$. Unlike the alkali salts, the ionic interaction strength of the alkaline earth metal salts increases with the increasing cation radius of alkaline earth metals probably due to the restricted mobility of the larger divalent cations. In addition, the ionic interaction strength of divalent transition metal salts is strongly related to the electron configuration of the cation, especially the configuration of 3$d$ orbital, indicating the formation of covalent bond with the sulfonate groups.
CHAPTER VIII
VISCOELASTIC BEHAVIOR OF ZINC SULFONATED EPDM - ZINC STEARATE
SHAPE MEMORY POLYMERS

8.1 Introduction

Ionomers are flexible polymers containing small amount (typically < 15 mol%) of covalently attached ionic groups.\textsuperscript{194} The polar ionic groups tend to form nano-sized ionic aggregates in the nonpolar medium due to their strong polar or ionic interactions. Those ionic aggregates, serving as physical crosslinks, provide the ionomer with excellent physical and mechanical properties of ionomers. Therefore, ionomers has been widely used in the industry as packaging films\textsuperscript{1}, polymer blends compatibilizers\textsuperscript{147}, and so on.

Unlike covalent crosslinks, those physical crosslinks (ionic aggregates) could relax, but only at higher temperatures or longer times through the so called “ion-hopping” process, in which the ion pairs dissociate from one aggregate and then “hop” to another, enabling the melt flow of ionomers.\textsuperscript{64} However, the presence of ionic aggregates restricts the motion of ionomer chains, and significantly delays the relaxation time.\textsuperscript{120, 121}

In order to promote the melt flow of ionomers, plasticizer is often added to weaken the ionic interaction. For instance, low molecular weight fatty acid or fatty acid salts (FA), such as zinc stearate (ZnSt), were found to be excellent plasticizer for sulfonated poly[eth-
ethylene-propylene-\(r\)-(5-ethylidene-2-norbornene)] (SEPDM) ionomers.\(^8^7\) FA can enhance its mechanical properties as a reinforcing filler at temperatures below the melting point, but promote its melt flow as an efficient plasticizer at higher temperatures due to the strong dipole-dipole interaction between FA and ionomer sulfonate groups\(^5^5, 8^7, 1^9^5\).

Recently, the blends of FA with Zn neutralized SEPDM (ZnSEPDM) was proposed as a promising candidate for shape memory polymers (SMP)\(^1^9^6\). In those compounds, the permanent network was provided by the physical ionic crosslinks, while the temporary network was provided by the micro-domains of FA and their strong interactions with ZnSEPDM ionomers. This approach was proven to be very versatile because the transition temperature, \(T_c\), can be easily adjusted through choosing an appropriate fatty acid or salt\(^1^9^6\). However, subsequent research\(^1^9^7\) revealed that there exists evident time-dependent relaxation of temporary shape: the shape recovery ratio decreased after aging temporary shape at room temperature for several days. Covalent crosslinking was recently found to be an efficient method to improve the shape recovery performance, while the mechanism for this improvement is still unknow.\(^1^9^8\)

We suspect that the shape recovery performance is related to the viscoelastic behavior, especially the creep recovery behavior, of the ZnSEPDM/FA ionomer compounds. However, there have been very limited studies concerned with the dynamics of this ionomer/FA system. For example, the dynamic rheological behavior of SPEDM/ZnSt compounds has been investigated by Agarwal et al.\(^6^5\) In this study, it was found that the incorporation of ZnSt increased the plateau modulus but significantly promoted the
terminal relaxation of the compound. In another study, Granick discovered that time
temperature superposition (TTS) failed for the relaxation modulus of ZnSEPDM/ZnSt
compounds at longer times, and the physical aging showed significant effect on the stress
relaxation behavior. Despite the above studies, a detailed understanding of the creep
behavior of ZnSEPDM/ZnSt compounds is still missing.

In order to illustrate the effect of covalent crosslinking on shape memory performance,
the creep behavior of ZnSEPDM/ZnSt compounds was systematically investigated at
various temperatures for different ZnSt loadings. The effect of ZnSt and covalent
crosslinking on the creep behavior was analyzed using the Burger model. Possible
mechanisms were proposed to illustrate the relation between creep behavior and shape
recovery performance.

8.2 Experimental section

This section described the preparation and the characterization of the ZnSEPDM/ZnSt
shape memory compounds.

8.2.1 Materials

EPDM with a backbone composition of 55% ethylene, 40% propylene, and 5% 5-
ethylidene-2-norborne [Mooney viscosity = 20 (ML,1 + 4, 100°C)] was obtained from
Exxon Chemical Co. SEPDM with a sulfonate concentration of 25 meq per one hundred
parts rubber (phr) was synthesized by sulfonating EPDM with acetyl sulfate in a 5wt%
dichloroethane solution. After the sulfonation, the sulfonic acid group was immediately
converted to zinc salt through the addition of excess zinc acetate dihydrate. Then the
obtained ZnSEPDM was washed several times with de-ionized water to remove excess zinc acetate and acetic acid.

ZnSEPDM/ZnSt compounds ranging in composition from 0-40wt% ZnSt were prepared by dissolving in a 95/5 (v/v) mixture of toluene and methanol. After evaporating the solvent, the obtained compounds was dried at air for one day, and then dried in vacuum oven at 50°C for 2 days. Afterwards, the compounds were vacuum compression molded at 150°C into thin films. For some of the samples, the films were covalent crosslinked through election beam radiation(EB, NEO Beam Alliance Ltd., Middlefield, OH) in air with a radiation dose of 200kGy\(^{198}\). The sample nomenclature used hereafter is SEPDM\(x-y\), where \(x\) and \(y\) represent the weight percentage of ZnSt and the EB radiation dose, respectively. For example, SEPDM20-0 denotes the uncrosslinked compound of ZnSEPDM with 20wt% ZnSt.

8.2.2 Materials characterization

Mechanical properties, shape memory and creep behavior of the compounds were measured by a dynamic mechanical analyzer (DMA, model Q800, TA Instruments) using tension mode. Specifically, the dynamic mechanical properties of the compounds was measured at a fixed frequency of 1 Hz with the temperature ramp from -100 to 200°C at 5°C/min. Shape memory properties were measured by shape memory cycle. A typical shape memory cycle can be illustrated as follows: Firstly, sample was heated from 30 to 110°C with a preload force of 0.01 N, after equilibrated at 110°C, the force was increased to predetermined value to stretch the sample, then the sample was cooled down to 30°C.
with load in order to fix the temporary shape. After equilibrating at 30°C, the force was removed, and the temporary shape was fixed. Afterwards, the deformed sample was reheated at 10°C /min to 110°C without any stress and maintain for 20min to allow strain recovery. Tensile creep tests were performed at isotherms from 20°C to 120°C in an interval of 10°C. A constant stress of 0.05MPa was applied for 30 min, followed by a 60 min recovery period. The strain was recorded and then converted to creep compliance.

The linear viscoelasticity of the compounds was investigated using a strain controlled rheometer (ARES-G2, TA Instruments) at a temperature range of 120 to 30°C and a frequency range of 0.01 to 100Hz. All measurements were conducted within the linear regime as determined from strain sweep. Shear creep measurements were also conducted on the ARES-G2 rheometer at either 80 or 120°C. The stress used in creep were carefully chosen without exceeding the limits of linear viscoelasticity.

8.3 Results and discussion

This section investigated the effect of covalent crosslinking on the viscoelastic and shape memory behavior of ZnSEPDM/ZnSt compounds.

8.3.1 Materials characterization

After 20wt% of ZnSt was incorporated into the SEPDM compounds, the melting point of ZnSt was decreased slightly from 125 to 120°C and its crystallinity decreased significantly to ~60%, due to the strong intermolecular interaction between ZnSt and the ionomer.198 Moreover, the incorporation of covalent crosslinking further decreased the crystallinity of ZnSt to ~53% when the EB dose increased from 0 to 200kGy.198
However, covalent crosslinking has little effect on the thermal stability of the SEPDM/ZnSt compounds. As shown in Figure 8.1, the crosslinked compound (SEPDM40-200) has nearly identical mass loss curve with that of the uncrosslinked compound (SEPDM40-0). Neat ionomer sample, SEPDM0-200, is quite stable until about 350°C, whereas ZnSt-filled compounds (SEPDMx-200, x=20, 30, 40) start to degrades at ~ 250°C because of the decarboxylation of ZnSt. From Figure 8.1, one can conclude that ZnSEPDM/ZnSt compounds are quite stable in the temperature range adopted in this study, in which they were kept between 20 and 120°C.

![Figure 8.1 Thermogravimetric analysis of SEPDMx-200 compounds. For uncrosslinked compounds, only SEPDM 40-0 was shown for clarity.](image)

Figure 8.2 shows the DMA results for the parent EPDM and SEPDMx-y compounds with and without covalent crosslinking. The neat EPDM begins to flow right after the
transition region ($T<50^\circ C$), where SEPDM<sub>x-y</sub> ($x = 0, 20, 30, 40$) compounds show evident elastic rubber plateau up to 100°C because of the presence of ionic groups. The fatty acid salt, ZnSt, increases the plateau modulus but decreases the modulus when it starts to melt at 100°C. With the increase of ZnSt loading, the plateau modulus (defined as the modulus at 50°C) increases from ~3.5MPa for neat SEPDM to nearly 45MPa for SEPDM40-y ($y=0$ or 200) as a consequence of reinforcement. At $T > 100^\circ C$, the storage modulus of SEPDM0-0 only decreases slightly, indicating that the ionic network is still robust at high temperatures. After EB crosslinking, SEPDM0-200 shows a relatively higher modulus at $T > 100^\circ C$ owing to the presence of the covalent network. However, for SEPDMx-0 ($x = 20, 30, 40$) compounds, the storage modulus decreases significantly at $T > 100^\circ C$, at which ZnSt melts and works as plasticizer<sup>198</sup>. For both SEPDM30-0 and 40-0 compounds, the storage modulus reaches the lower limit of the instrument at $T > 150^\circ C$. It means the ionic network is almost broken because the ion hopping process is greatly enhanced by the molten ZnSt. Upon covalent crosslinking, the storage modulus of SEPDMx-200 ionomers becomes much higher than their correspondingly uncrosslinked compounds (SEPDMx-0) at higher temperature ($T > 150^\circ C$). Although the ionic network does not persist at high temperatures, the covalent network prevents the compounds from melt flowing.
8.3.2. Shape memory behavior

In order to investigate the consistency of shape memory behavior of SEPDM\textsubscript{x-y} compounds, six consecutive shape memory cycles were measured by DMA for both SEPDM 30-0 and SEPDM30-200 compounds, as shown in Figure 8.3a and 8.3b. When the sample was heated to 110°C, it was deformed. Afterwards the temperature was decreased to 30°C to fix the temporary shape. After removing the force (unloading), the deformed sample was reheated to 110°C to recover the original shape. The shape fixation and recovery ratio were calculated and listed in Table 8.1 using the following equations,\textsuperscript{200} in which $\varepsilon_s$, $\varepsilon_f$, $\varepsilon_r$, and $N$ represent the strain after stretching (before unloading), strain after unloading, strain after the recovery, and the cycle number, respectively.

$$R = \frac{\varepsilon_f(N) - \varepsilon_r(N)}{\varepsilon_f(N) - \varepsilon_r(N-1)} \times 100\%$$

(8.1)
The reproducibility of the SMCs is quite good except for the small irreversible extension of the sample during the first cycle. For both SEPDM30-0 and 30-200 compounds, a \( R \) of > 90% can be observed except in the first cycle of SEPDM30-0. Upon covalent crosslinking, the recovery ratio \( R \) is significantly increased. For the first cycle, \( R \) is increased from 77% for SEPDM30-0 to 97% for SEPDM30-200, afterwards, the \( R \) of the SEPDM30-200 becomes nearly 100%, compared to the \( R \) of ~95% for the uncrosslinked sample (SEPDM30-0). However, the shape fixity decreases from ~80% in SEPDM30-0 to ~70% in SEPDM30-200. After EB crosslinking, the retraction force during the fixing part becomes much higher due to increased crosslinking density, thus the temporary network isn’t strong enough to fix the temporary shape, especially when the crystallinity of ZnSt was also reduced upon crosslinking.\(^{198}\) In other words, covalent crosslinked sample has a higher retraction force but a weaker temporary network. Therefore, when the external force was removed, the covalent crosslinked sample will retract more to relax the internal stress, leading to a lower shape fixity \( F \).

An ideal shape memory cycle would give a value of \( F \) and \( R \) of 100%. In an ideal scenario, there isn’t any creep at the point when the load is applied or held. However, in Figure 8.3a, a significant increase in strain can be observed when the load is applied at 110°C. In addition, during the cooling process, the strain is further increased under load. The increment of strain in both cases is attributed to the creep behavior of the shape.

\[
F = \frac{\varepsilon_f(N)}{\varepsilon_s(N)} \times 100\% \tag{8.2}
\]
memory polymers. Similar behavior has been reported previously in both ZnSEPDM/ZnOl\textsuperscript{197} and SPEEK/FA\textsuperscript{201,202} systems. In general, there are two kinds of creep: one is the creep of the temporary network, and the other is the creep of permanent network. Only the latter is detrimental for the shape recovery.

As shown in Figure 8.3a, even the strain was increased from about 10% to 16% in the holding and cooling stage, only a few portions of it could not recover. The total irrecoverable strain $\varepsilon_{ir}$, defined as the amount of irrecoverable strain, was calculated and summarized in Table 8.1. Compared with the shape recovery ratio $R$, it is better to use the irrecoverable strain to quantify the recovery performance throughout the many consecutive shape memory cycles. For both SEPDM30-0 and 30-200 compounds, the irrecoverable strain increases with the cycle number, indicating the creep of the permanent network for every shape memory cycle, which is consistent with the trend observed in Nafion\textsuperscript{203}. For SEPDM30-0, the irrecoverable strain is 3.31% for the first cycle, and gradually increases to 6.22% for the sixth cycle. However, the irrecoverable strain for the SEPDM30-200 sample is reduced to 0.45% for the first cycle. Even after six shape memory cycles, the irrecoverable strain is only 0.84%, nearly an order of magnitude lower than that of uncrosslinked sample. In other words, the ionic network, the previous believed “permanent” network, creeps with the shape memory cycles, and this creep can be significantly reduced via covalent crosslinking, which is consistent with our previous findings\textsuperscript{198}. 
Figure 8.3 Six consecutive shape memory cycles for (a) SEPDM30-0, and (b) SEPDM30-200 composites.
Table 8.1 shape fixation and recovery ratio for shape memory data shown in Figure 8.3

<table>
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<th>Cycle #</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>84</td>
<td>84</td>
<td>84</td>
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<tr>
<td>R(%)</td>
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<td>$\varepsilon_{ir}$(%)</td>
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<td>0.70</td>
<td>0.74</td>
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8.3.3 Tensile creep behavior

To understand the creep behavior of SEPDM compounds and its relation to shape memory behavior, short time isothermal creep experiments were conducted on both uncrosslinked and covalent crosslinked samples. In a creep experiment, a constant stress, $\sigma_0$, was applied at $t = 0$ up to a predetermined creep time $t = t_0$, and the time dependent strain $\varepsilon(t)$ was measured. The creep compliance, $D(t)$, was defined as

$$D(t) = \frac{\varepsilon(t)}{\sigma_0} \quad (8.3)$$

At $t = t_0$, the stress was set to zero, and then the sample was allowed to recover.

Numerous models have been proposed to analyze the creep behavior of viscoelastic materials. Of those models, the Burger model, a combination of Maxwell and Voigt models in series, is the simplest and most widely used. In the Burger model, the creep compliance can be expressed as
\[ D(t) = D_0 + D_1 \left(1 - e^{-t/\tau}\right) + \frac{t}{\eta_0} \]  

(8.4)

in which \( D_1 = 1/E_1 \) and \( \tau = D_1 \eta_1 \) comes from the Voigt element, describing the retardation process. \( E_1 \) and \( \eta_1 \) are the modulus and viscosity of the Kelvin spring and dashpot, respectively, while the initial creep compliance \( D_0 = 1/E_0 \) and viscosity \( \eta_0 \) correspond to the spring and dashpot in Maxwell element. In general, the three terms in the equation represent the instantaneous deformation, retarded deformation, and viscous flow of a material, respectively. The first two terms describe the recoverable compliance, while the latter accounts for the irrecoverable creep compliance.

Figure 8.4a shows the typical creep strain response of SEPDM0-0 and SEPDM0-200 ionomers. For both samples, the creep strain increases with the increasing \( T \) because of the enhanced chain mobility. However, the influence of covalent crosslinking varies for different \( T \). At low temperature, e.g. \( T = 10 \) and \( 30^\circ\text{C} \), covalent crosslinking slightly increases the creep strain due to the polymer degradation induced by EB irradiation\(^{204}\). Meanwhile, the creep strain at higher temperatures (\( T = 80-120^\circ\text{C} \)) was reduced by covalent crosslinking, and this reduction in creep strain increases with increasing \( T \). At higher temperatures, the effect of degradation becomes less important because the creep behavior is mainly associated with the long time relaxation process. In other words, the presence of covalent crosslinking increases the relaxation time considerably, thus reducing the creep strain.

If 20wt% ZnSt was added, the effect of covalent crosslinking on the creep behavior
becomes more evident. As exhibited in Figure 8.4b, at 80°C, the creep strain of SEPDM20-0 after 30min is only 1.7%, well below the ~2.8% creep strain of neat SEPDM0-0. However, at 120°C, the creep strain of SEPDM20-0 increases rapidly to a value of ~34%, which is significantly larger than the ~4% strain of SEPDM0-0. The filler (ZnSt), acts as a reinforcer at $T < 80^\circ$C to decrease the creep strain, but works as a plasticizer to increase the creep strain when it melts at higher $T$. Similar to neat ionomers (SEPDM0-0), at low temperatures, the creep strain increases slightly upon covalent crosslinking due to the degradation of polymer chains, while at high $T$, e.g. 120°C, it is significantly reduced upon the crosslinking, decreasing from 34% to only 9.6% after 30 min. However, SEPDM20-200 still has a creep strain of 9.6% at $t = 30$min, which is above two times that of SEPDM0-0.
Figure 8.4 Time evolution of creep strain under different temperatures for (a) SEPDM0-0 (filled symbol) and SEPDM0-200 (open symbol), (b) SEPDM20-0 (filled symbol) and SEPDM20-200 (open symbol) compounds. Lines are shown for guidance.

In order to quantify the effect of covalent crosslinking, the four-element Burger model was adopted to fit the creep data in this study. Figure 8.5 shows the creep compliance of
SEPDM40-0 and SEPDM40-200 compounds under constant stress of 0.05MPa at different temperatures as examples. The same axis scale was used for both graphs, from which a decreased creep compliance can be clearly observed from the crosslinked sample. For example, at $T = 120^\circ$C, the creep compliance at 30min decreases almost an order of magnitude, from $10^{-5}$ to $10^{-6}$Pa$^{-1}$ when covalent crosslinking is introduced. In addition, the creep compliance of SEPDM40-200 is gradually reaching a plateau, while that of SEPDM40-0 still increases with a nearly constant slope. In addition to crosslinking, the temperature also exhibits significant influence on the creep behavior. When $T < 90^\circ$C, the increment in creep compliance within a 10°C increase is quite small (see Figure 5a and 5b). However, when $T \geq 90^\circ$C, the creep compliance is greatly enhanced upon the increasing $T$. This temperature effect can be ascribed to the melting of ZnSt crystals, which decreases the modulus and enhances the creep deformation. In a previous study$^{198}$, the melting point of ZnSt was determined to be $\sim 120^\circ$C, but this value is only the temperature at melting peak. Actually ZnSt begins to melt at 90°C.$^{198}$ As discussed above, molten ZnSt is a very good plasticizer for ZnSEPDM. When it melts, it can weaken the ionic interaction and promote the viscous flow.
Even though the Burger model is almost the simplest creep model, it still provides a very good fit for all the compounds with the correlation coefficient $R$ larger than 0.99.
Those fitting parameters are summarized in Figure 8.6. For SEPDM0-0 and SEPDM0-200 samples, \( D_0 \) increases slightly with \( T \) owing to the thermal softening the polymer (Figure 8.6a). \( D_0 \) is slightly higher for SEPDM0-200 than its uncrosslinked counterpart at low temperatures, which is consistent with Figure 8.4. For all ZnSt filled compounds, \( D_0 \) and the slope of \( D_0 \) against \( T \) increases with increasing \( T \), especially when \( T > 90^\circ C \) (where ZnSt crystals melts). When \( T < 90^\circ C \), \( D_0 \) decreases with the increase of ZnSt loadings due to its reinforcement effect. However, at higher \( T \), such as \( T = 120^\circ C \), the compounds exhibit a higher \( D_0 \) than that of the neat ionomer, and the difference between different ZnSt loadings decreases. The reinforcement effect of ZnSt at low temperature and its plasticization effect at higher temperatures is responsible for the difference in \( D_0 \).

The parameters \( D_1 \) and \( \tau \), shown in Figure 8.6b and 8.6d, represent the reciprocal of the spring modulus and dashpot viscosity in Kelvin element, respectively. \( D_1 \) increases with increasing \( T \) for all the samples. The \( D_1 \) of the SEPDM\( x-y \) \((x > 0)\) compounds is lower than that of neat ionomer (SEPDM0-y) at lower temperatures but higher than it at higher ones; which is similar with trend observed in the instantaneous creep compliance \( D_0 \). Covalent crosslinking has little influence on \( D_1 \) at low \( T \), though decreases it when \( T > 90^\circ C \). As for retardation time \( \tau \), there is no clear trend observed in the Figure 8.6d. Considering that this system contains both ionic nano-phase separation and ZnSt crystals, a single retardation time may not be able to fully describe those different relaxation processes. A possible mechanism for this retardation process is the temporary network formed by ZnSt crystals and ionic aggregates. At lower \( T \), the increased ZnSt concentration provides a stronger
temporary network and thus decreases $D_1$. Whereas covalent crosslinking has little effect on $D_1$, indicating that the temporary network is not significantly affected by the covalent crosslinks. When ZnSt melts, this temporary network disappears, and the effect of covalent crosslinking becomes evident. It increases the modulus and decreases $D_1$ (see the arrow in Figure 8.6b).

Figure 8.6 Temperature dependence of the four parameters in the Burger model. (a) Instantaneous compliance $D_0$; (b) Retardant compliance $D_1$; (c) Permanent flow viscosity $\eta_0$, (d) Retardation time $\tau$.

Among the four parameters of the Burger model, $\eta_0$ is the most important because it accounts for the viscous flow and the irrecoverable deformation, which is the origin for the irrecoverable strain in the shape memory cycles. A larger $\eta_0$ means a smaller viscous
deformation, thus a higher shape recovery ratio $R$. Figure 8.6c compares $\eta_0$ for different ZnSt loadings. At low temperatures, $\eta_0$ is higher for filled compounds than neat SEPDM. When ZnSt crystals start to melt at $T = 90^\circ C$, $\eta_0$ becomes much smaller for filled compounds due to the plasticization effect of ZnSt. As shown by the arrow in Figure 6c, crosslinked compounds exhibit significant higher viscosity $\eta_0$ at $T > 90^\circ C$ than their uncrosslinked samples. At $120^\circ C$, this increment of $\eta_0$ reaches nearly 2 orders of magnitude, from $10^8$Pa.s (SEPDM40-0) to $10^{10}$Pa.s (SEPDM40-200). It indicates that the covalent network could significantly enhance the resistance to viscous flow even the ionic aggregate is plasticized with such high loadings of ZnSt. Furthermore, the irrecoverable creep strain, which is inversely proportional to the $\eta_0$, can be efficiently suppressed. It means that the irrecoverable creep phenomenon observed in shape memory cycle is probably related to the viscous deformation of ionomer. Even ZnSt provides a temporary network to form SMP, it also brings detrimental effect to the physical ionic network due to its plasticization effect.

To better analyze the long term performance of shape memory polymers, time temperature superposition principle (TTS) was adopted to study and predict the creep behavior over long periods of time. However, TTS fails for all the compounds due to the presence of multiple relaxation processes with different temperature dependences. Figure 8.7 shows the pseudo-master curves, where their creep compliance was matched at short times, of both SEPDM20-0 and SEPDM20-200 compounds. Before the curves were shifted horizontally, the creep compliance was multiplied by $T/T_i$ to take the temperature effect into consideration, with $T_i$ set at $20^\circ C$. As shown in Figure 8.7a, deviations from the master
curve can be clearly observed. It is not surprising that the TTS principle fails for these complex multicomponent compounds. Similar phenomenon was also observed in a previous study of the same ZnSEPDM/ZnSt system\textsuperscript{199}. From the pseudo-master curves, a clear trend can also be observed that the crosslinked sample (SEPDM20-200) exhibits a significantly lower creep compliance than uncrosslinked one (SEPDM20-0), especially at higher times owing to suppression of viscous flow.

Figure 8.7 Creep compliance pseudo-master curves for SEPDM20-0 (a) and SEPDM20-200 (b) at $T_r = 20^\circ$C

8.3.4 Dynamic oscillatory shear behavior

In order to further investigate the effect of covalent crosslinking on the viscoelastic behavior of SEPDM$_{x-y}$ compounds, dynamic shear experiments were performed at different temperatures. As shown in Figure 8.8a, storage modulus $G'$ and loss modulus $G''$ of neat ionomers (SEPDM0-$y$) are reduced slightly after EB crosslinking. In addition, the slope of $G'$ at low frequencies (the exponent $n$ in $G' \propto \omega^n$) decreases slightly from 0.09 for
SEPDM0-0 to 0.07 for SEPDM0-200. Typically, the dynamic moduli at higher frequencies are related to the bulk properties of the polymer chain, which is associated with faster relaxation, whereas the moduli at lower frequencies are mainly dependent on slower relaxation. The slope $n$ is often associated with the microstructure: a slope of 0 means an elastic network, while a slope of 2 indicates viscous fluid. Moreover, the decrease of slope in $G'$ means the increase of the terminal relaxation time. From this, we can conclude that covalent crosslinking can suppress the viscous flow of the neat ionomer although it slightly decreases the dynamic moduli. The effect of covalent crosslinking on dynamic moduli is similar to that of creep behavior, but a difference still exists. As exhibited above, the creep strain of SEPDM0-200 is higher than that of SEPDM0-0 only at $T < 40^\circ$C, but the dynamic moduli of SEPDM0-200 is lower for all temperatures. The time scale for typical dynamic experiments is often in the range of 0.01-100s (associated with a frequency range of 0.01-100Hz), while in creep experiment, this time scale can be extended to 1800s for 30 minutes of creep test. Thus the increase of terminal relaxation time due to the covalent crosslinking is more evident in a creep test. In a dynamic test, only the short relaxation times are detected, which mainly shows the effect of chain degradation, whereas in the creep test, the increase of terminal relaxation time becomes dominating especially at higher temperatures.

Compared to neat ionomers, the reinforcement effect of ZnSt at $T < 90^\circ$C and its plasticization effect at $T > 90^\circ$C can be clearly seen in Figure 8.8a and 8.8b. At $T < 90^\circ$C, the dynamic moduli of SEPDM40-0 and SEPDM40-200 samples are one order of magnitude higher than that of SEPDM0-$y$ ionomers ($10^6$ Pa vs $10^5$ Pa). While at $T = 120^\circ$C,
the \( G' \) decreases from \( \sim 2 \times 10^5 \) Pa for SEPDM0-y to less than \( 10^5 \) Pa for SEPDM40-y. Due to the plasticization effect of ZnSt, the slope of \( G' \) against frequency, \( n \), at \( T = 120^\circ C \) increases significantly upon the addition of ZnSt. Compared to the neat SEPDM0-0, the addition of 40wt% ZnSt increases \( n \) from 0.09 to 0.27, indicating an accelerated terminal relaxation due to the plasticization effect of ZnSt. The incorporation of covalent crosslinking slightly decreases the dynamic modulus of SEPDM40-y compounds, but significantly reduces the slope \( n \) from 0.27 for SEPDM40-0 to only 0.13 for SEPDM40-200. Although, covalent crosslinking shows a weaker effect on the dynamic moduli than the creep compliance, the suppressed melt flow at high \( T \) can still be clearly observed.
Figure 8.8 Frequency dependence of storage moduli $G'$ (filled symbol, or solid line) and loss moduli $G''$ (open symbol, or dashed line) for (a) SEPDM0-0 (symbol) and SEPDM0-200 (line), (b) SEPDM40-0 (symbol) and SEPDM40-200 (line). The dark red and yellow solid line are associated to the terminal slope of $G'$ at 120°C.
8.3.5 Shear creep behavior

The creep behavior discussed above is tensile creep under high stress (0.05MPa), which is comparable to the stress used in shape memory cycles. However, this stress is already beyond the linear viscoelastic region. The shear creep behavior of SEPDM/ZnSt compounds within linear viscoelastic region was also investigated. Figure 8.9 shows the comparison of shear creep and tensile creep behavior of SEPDM30-x compounds as an example. A reduction of shear compliance at $T = 80^\circ$C and $120^\circ$C can be clearly observed after covalent crosslinking, and this reduction is much higher for that of $120^\circ$C, which is consistent with tensile creep behavior observed in Figures 4 and 5. However, at $120^\circ$C, shear creep compliance (green symbol) is 10 times higher than the tensile creep compliance (orange line). There are two main reasons for this big difference: one is the difference between tensile mode and shear mode, and the other is the non-linear creep behavior in the tensile mode. The stress used in the tensile creep is quite high (0.05MPa), which is beyond the linear viscoelasticity region. In the nonlinear region, a much lower creep compliance is often observed. Although there is a big difference in the values of shear and tensile creep, covalent crosslinking indeed suppresses both shear and tensile creep compliance significantly, especially the creep at longer times and higher temperatures.
Figure 8.9 Time dependence of shear creep compliance for SEPDM30-0 (filled symbol) and SEPDM30-200 (open symbol). The stress used in creep are 3000 Pa and 1000 Pa for 80 and 120°C, respectively, and both of them are within linear viscoelastic region. Tensile creep compliance of SEPDM30-0 (orange solid line) and SEPDM30-200 (orange dash line) under 0.05 MPa at 120°C are shown for comparison.

8.3.6 Proposed mechanism

Although it is difficult to construct a quantitative relation between creep compliance with shape memory performance, a qualitative relation can still be made from the above discussions. As shown in Figure 8.10a, when uncrosslinked SEPDMx-0 compounds are heated up, ZnSt starts to melt, and it swells the ionic aggregates and weakens the ionic interaction between zinc sulfonate groups. This is consistent with our previous study that the ionic scattering peak moved to higher $q$ when ZnSt melts, indicating the increase of the size of the ionic aggregates. Therefore, when ZnSt melts, the terminal relaxation time of the ionomer is significantly reduced, and the ion-hopping process is greatly accelerated. During the loading stage, the ionic group (shown as cyan dot in Figure 8.10a) may hop to
the neighbor aggregates, and it will probably not come back to its original aggregate in the recovery stage. Therefore, the memory of the original chain conformation loses. In other words, the believed ‘permanent’ ionic network creeps, and this creep is irrecoverable. However, when covalent crosslinking (shown as red line) is introduced to this compound, even the ionic interaction is significantly weakened; the ionic group can’t move out the original aggregate due to the confinement of crosslinking (Figure 8.10b). In this case, the ion-hopping process can be sufficiently suppressed, thus enhancing the shape recovery performance.

8.4 Conclusions

In this work, the viscoelastic behavior of ZnSEPDM/ZnSt shape memory polymers was investigated. Even the ionic network was believed to be a robust “permanent” network, the addition of ZnSt could deteriorate the ionic interaction when it melts as a plasticizer. After fitting creep data with the Burger model, covalent crosslinking was found to increase the melt viscosity, reduce the irrecoverable viscous deformation, and thus improve the
shape recovery performance. Therefore, the effect of covalent crosslinking can be ascribed to the suppressed ion-hopping process of the ionomer. While the ionomer/FA system is a versatile method to prepare SMP with different transition temperatures, certain degrees of covalent crosslinking are still needed to reduce the creep of “permanent” ionic network.
CHAPTER IX

SUMMARY AND FUTURE WORK

9.1 Summary

The major objective of this dissertation is to understand and predict the rheological behavior of random ionomers. In order to avoid the effect of chain entanglement, oligomeric sulfonated polystyrene (SPS) ionomers were selected as a model system to investigate the effect of ionic content (sulfonation degree), neutralization degree, the type of metal cation, and the mixing of the metal cations on the rheological behavior of ionomers. A reversible gelation model was then developed to predict the LVE behavior of SPS ionomers, and a good agreement was achieved between experimental data and model predictions for all SPS ionomers investigated.

In the first part, two oligomeric PS precursors with both molecular weight below the entanglement molecular weight ($M_c$) were sulfonated by different degrees of sulfonation ($p$) following the Makowski’s method. After neutralizing the SPS acid derivatives into different alkali salts, the effects of sulfonation degrees and metal cation on the LVE behavior of SPS ionomers were investigated. The gel point of random ionomers was determined as $p = p_c$, where the ionomer contains one ionic group per chain on average. Below the gel point, $p < p_c$, ionomers show typical sol-like relaxation behavior with loss
modulus higher than storage modulus at frequencies below the glass transition. Compared to the PS precursors, the increase of sulfonation degree $p$ delays the Rouse relaxation process due to the presence of ionic interaction. Close to the gel point, $p \sim p_c$, three characteristic power law relaxations occur: mean field behavior, $G'(\omega) \sim G''(\omega) \sim \omega^1$, at high frequencies, critical percolation behavior, $G'(\omega) \sim G''(\omega) \sim \omega^{2/3}$, at intermediate frequencies, and terminal relaxation behavior $G'(\omega) \sim \omega^2, G''(\omega) \sim \omega^1$. Above the gel point, $p > p_c$, a plateau emerges in the $G'$, and the plateau modulus increases with increasing $p$ due to the increased density of the ionic network.

TTS works quite well for $p < p_c$, but fails in the terminal region of $G'$ for $p \sim p_c$, and in the valley of $G''$ for $p > p_c$. The failure of TTS was attributed to the overlap of two relaxation processes with different temperature dependences: the Rouse relaxation and the ionic dissociation. The increase of the radius of alkali cations does not significantly affect the LVE behavior of ionomers with $p < p_c$, but it significantly accelerates the terminal relaxation of ionomers with $p \sim p_c$ or $p > p_c$. Based on the mean field theory of Rubinstein and Semenov, a reversible gelation model was developed through incorporating a transition from mean-field to critical percolation at the Ginzburg point. With only two parameters, the Rouse relaxation time of the Kuhn segment $\tau_0$ and ionic dissociation time $\tau_s$, the reversible gelation model predicts well the LVE behavior of SPS ionomers with different $p$ and alkali cations.

In the second part, the LVE behavior of the blends of two SPS ionomers with different degrees of sulfonation and metal cations was investigated and compared with the
predictions from reversible gelation model. In these binary blends, one ionomer component has a degree of sulfonation \( p \ll p_c \), while the other ionomer has \( p > 2p_c \). This enables us to control the average sulfonation degree of the blends, \( \bar{p} \), in the range from far below the gel point to far above. The binary ionomer blends show identical gel point and similar power law relaxation with that of neat ionomers. However, at the same ionic concentration, the ionomer blends exhibit a longer terminal relaxation time but a lower plateau modulus than neat ionomers due to their broader relaxation time spectrum. This broad relaxation spectrum of binary ionomer blends is probably originated from their broad distribution of ionic groups along the ionomer chains.

In addition, the effect of the mixing of different alkali cations on the LVE behavior was successfully quantified by a simple mixing rule: the average ionic dissociation frequency, i.e. the reciprocal of the ionic dissociation time, of the blend is the weighted average of the ionic dissociation frequency of the two component cations. With this mixing rule incorporated, the reversible gelation model predicts well the LVE of ionomer blends with different \( \bar{p} \) and different combinations of cations. Although the model under-predicts the terminal response of \( G' \) for \( \bar{p} < p_c \), it provides an excellent prediction the terminal relaxation time of ionomer blends with \( \bar{p} > 2p_c \), where the terminal relaxation is mainly controlled by the ionic dissociation.

In the third part, the nonlinear rheological behavior of SPS ionomers with \( p < p_c, p \approx p_c, \text{and} \ p > p_c \) was investigated by steady shear and startup shear. When \( p < p_c \), the ionomer exhibits typical shear thinning behavior at high shear rates. When \( p > p_c \), following the
Newtonian region, evident melt fracture occurs at high shear rates. Only when $p \sim p_c$, shear thickening emerges between the Newtonian and shear thinning regions. The shear thickening behavior is accompanied by the absence of nonlinearity in the first normal stress difference coefficient, and the appearance of strain hardening in the growth viscosity during the startup shear. The magnitude of shear thickening increases with the decrease of temperature, the cation radius, and the molecular weight of the PS precursor, due to the increased contrast between the ionic dissociation time $\tau_s$ and the Rouse relaxation of the Kuhn segment of the precursor chain, $\tau_0$.

In the fourth part, the LVE behavior of partially neutralized SPS ionomers was investigated with respect to different sulfonation levels ($p$) and neutralization degrees ($x$). For a given $p$, the plateau modulus is independent of the neutralization degree $x$, and the partially neutralized SPS ionomers show similar LVE behavior with the blends of fully neutralized SPS ionomer and unneutralized SPS ionomer containing the same amount of metal cation. This indicates that both metal sulfonates and sulfonic acid groups are condensed in the same ionic aggregates and both contribute to the formation of the ionic network. At the same metal cation content, the increase of extra sulfonic groups delays the Rouse segmental relaxation, but significantly accelerates the terminal relaxation, exhibiting a plasticization effect on the ionic dissociation.

The reversible gelation model works reasonably well for all ionomers except an over-predicted plateau modulus. The obtained ionic dissociation time $\tau_s$, however, is mainly controlled by the neutralization degree $x$ rather than the ionic concentration $p$. The increase
of $x$ significantly increases the $\tau_s$ and zero shear viscosity $\eta_0$ of ionomers, especially, near the complete neutralization, which can be attributed to the increased ionic interaction strength due to the decrease of polar acid groups.

The dielectric behavior of partially neutralized SPS ionomers was also investigated, and it was found that the amplitude of the $\alpha$ relaxation is controlled by the amount of polar acid groups until $x \geq 90$, where $\tau_s$ and $\eta_0$ experience rapid increase with the increasing $x$. Based on the Onsager equation, the localized dielectric constant $\varepsilon_s$ within the ionic aggregates was determined as a function of $x$. After incorporating $\varepsilon_s$ into the activation energy of the ionic dissociation, the $x$ dependence of the $\tau_s$ was successfully predicted, indicating that the major plasticization effect of the polar acid groups is the softening of the ionic interaction between metal sulfonate groups.

In the fifth part, SPS ionomers with $p < p_c$, $p \sim p_c$, and $p > p_c$ were neutralized by divalent metal cations, and their LVE behavior was investigated and compared with the model predictions. For all divalent metal cations, the ionomers show similar LVE behavior with that of alkali salts: exhibiting a sol-like relaxation for $p < p_c$, characteristic power law relaxations for $p \sim p_c$, and a plateau in $G'$ with the plateau modulus independent of metal cation for $p > p_c$. Unlike the alkali cations, the alkaline earth metal cations exhibit an increase of $\tau_s$ with the increasing cation radius probably due to the restricted mobility of the larger divalent cations. In addition, the $\tau_s$ of divalent transition metal cations is strongly related to their electron configuration, especially the configuration of $3d$ orbital, suggesting the formation of covalent bonds with the sulfonate groups.
In the sixth part, the viscoelastic behavior of the SEPDM/ZnSt shape memory compounds with and without covalent crosslinking was investigated under different temperatures and ZnSt loadings. The incorporation of ZnSt decreases the creep compliance of the compound at temperatures below the melting point, but significantly increases the creep compliance and promotes the melt flow when ZnSt melts at high temperatures due to its plasticization effect. Covalent crosslinking slightly increases the creep compliance of the SEPDM/ZnSt compound at low temperatures because of the electron beam irradiation induced polymer degradation, but significantly reduces the creep compliance at high temperatures. After fitting with the Burger model, it was found that the covalent network could sufficiently suppress the plasticization effect of ZnSt, thus decrease the irrecoverable creep compliance and improve the shape recovery performance.

9.2 Future work

The possible subject for the future research was summarized and discussed in this section.

9.2.1 Effect of plasticizers on the rheology of oligomeric ionomers

Our studies have shown that the LVE behavior of SPS ionomers is strongly affected by the increase of localized dielectric constant within the ionic aggregates due to the presence of polar acid groups. Although we were able to qualitatively predict the change of ionic dissociation time from the dielectric constants, the low values of the dielectric constant restricts the detailed study of their dielectric relaxation behavior. In order to further explore the dielectric and viscoelastic behavior of ionomers, it would be of interest to
examine the effect of plasticizers on the LVE behavior of SPS ionomers. A series of plasticizers with different dielectric constants can be selected, such as nonpolar plasticizer dioctyl phthalate (DOP), polyethylene glycol (PEG), and polar plasticizer glycerol. So that the plasticization effect can be selectively applied to either polymer backbone, the ionic aggregates or both. Then the effect of plasticizers on the dielectric and viscoelastic behavior as well as the relation between dielectric relaxation and ionic dissociation can be determined.

9.2.2 Effect of neutralization degree on the zinc and lithium neutralized SPS ionomers

A lot of studies have demonstrated that the Zn salts have the lowest melt viscosity among all metal cations. However, in partially neutralized PEMA ionomers, the Zn salt exhibits a higher viscosity than that of Na salt under the same neutralization degree. It was postulated that Zn salts might be less associated with the acid groups, which weakens the plasticization effect of polar acid groups. Therefore, it would be of interest to study effect of neutralization degree on the Zn salts of SPS ionomers. The result from this study will provide a molecular level understanding for the superior mechanical properties of Zn neutralized ionomers. Similarly, the interaction between acid groups and Li salts would also be an interesting subject of further research as both H and Li cations are among the smallest cations in the world. The understanding of the LVE behavior of Li neutralized SPS will be very helpful for the development of polymeric single-ionic conductor aiming for the battery applications.
9.2.3 Rheology of ionomer blends with monovalent and divalent metal cations

Previous study shows that the divalent cation neutralized ionomers exhibit quite different LVE behavior with that of alkali metal salts. However, the exact reason for this different LVE response is still unknown. In addition, our study of the ionomer blends only focused on the mixing of alkali cations. The validity of the linear mixing rule of the ionic dissociation frequency was not tested for the blends of monovalent and divalent metal cations. It would be of interest to study the mixing of alkali cations with alkaline earth metal cations or transition metal cations on the LVE behavior of SPS ionomers. Furthermore, the mixing of two divalent or even multivalent cations might also be an interesting subject of research for the dynamics of ionomers.

9.2.4 Rheological model for entangled ionomers

The major purpose of using oligomeric sulfonated polystyrene system is to achieve a thorough understanding of the effect of ionic interaction on the dynamics of random ionomers with the absence of the chain entanglement. However, these oligomeric ionomers have poor mechanical properties, which make them unsuitable for the industrial applications. Therefore, it would be of interest to extend those rules discovered and models developed in the oligomeric ionomers to the dynamics of entangled ionomers. For instance, the effect of ionic interaction on the rheology of entangled SPS ionomers could be thoroughly studied with respect to different ionic contents, neutralization degrees and metal cations. Furthermore, based on the concept of sticky Rouse model, a sticky reptation model could also be developed to predict the LVE behavior of entangled ionomers.
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