DIELECTRIC SPECTROSCOPY INVESTIGATION OF ION-CONTAINING
AND INTERMOLECULAR HYDROGEN-BONDED POLYMER SYSTEMS

A Thesis in
Materials Science and Engineering

by

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Ion-containing and intermolecular hydrogen-bonded polymers are used widely in a variety of industrial and commercial applications, from food packaging to battery electrolytes to pharmaceuticals. Yet the dynamics of these polymers, which are both complex and important to the application, are poorly understood. This thesis provides the first systematic study of the dynamics of several ion-containing and intermolecular hydrogen-bonded polymers by broadband dielectric relaxation spectroscopy. The systems under consideration include sulfonated polystyrene (SPS) in acid (SPS-H) and neutralized forms, and mixtures of poly(2-vinylpyridine) (P2VPy) with lithium perchlorate (LiClO₄) and low molecular weight phenolic molecules. Dynamic mechanical analysis, Fourier transform infrared spectroscopy, differential scanning calorimetry, small-angle X-ray scattering and wide-angle X-ray diffraction were employed in a complementary role.

Multiple relaxations were generally observed at high temperatures. For SPS ionomers, the segmental process, Maxwell-Wagner-Sillars interfacial polarization, and electrode polarization were detected. Three relaxations were also found in spectra of SPS-H, attributed to the segmental process, hydrogen bond association/dissociation, and electrode polarization.

Three dielectric relaxations above the segmental process were observed for P2VPy - LiClO₄ mixtures: ion-mode relaxation, slow hindered segmental relaxation and electrode polarization. However, only electrode polarization was observed above the segmental relaxation for all P2VPy – small phenolic molecule mixtures, except P2VPy + 10 mol % 2,3,3,4,4,5-hexahydroxybenzophenone. This mixture exhibited an additional
relaxation due to Maxwell-Wagner–Sillars interfacial polarization, arising from the existence of phase-separated complexes within the P2VPy matrix.

Sub-$T_g$ local relaxations were suppressed by ionic intermolecular interactions for SPS ionomers and P2VPy – LiClO$_4$ mixtures. Intermolecular hydrogen bonding also suppressed the local relaxation in P2VPy – small phenolic molecule mixtures by decreasing the mobility of the pyridine-side groups. Both the concentration of small phenolic molecules and the number of hydroxyl groups per molecule played an important role in suppression of the local relaxation, which was significant for all mixtures where the small molecules contained more than one hydroxyl group per molecule.
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Chapter 1

Introduction

1.1 Motivation

Polymer systems with strong intermolecular interactions such as hydrogen bonds or ionic aggregates exhibit a rich assembly of dynamics. Previous investigations have shown that, under the appropriate conditions, dielectric relaxation spectroscopy (DRS) is an extremely powerful tool to probe polymer dynamics in the presence of intermolecular bonding. For example, hydrogen bonding in polymer blends such as poly(vinylphenol) (PVPh)-poly(ethyl methacrylate) strongly suppresses dynamical heterogeneity [1], which is difficult to observe by other techniques. It was also found that poly(vinyl ethyl ether)-PVPh blends exhibit coupled segmental dynamics in the presence of sufficient intermolecular hydrogen bonds [2]. DRS can probe not only the segmental dynamics related to the dynamic glass transition, but also the relaxations above the dynamic glass transition, such as relaxations that occur in liquid crystalline polyurethanes and polycarbonates [3,4], as well as the secondary relaxations that arise from local dipole motion in the glassy state. The local β process of poly(2-vinylpyridine) (P2VPy) is significantly suppressed upon blending with PVPh and the introduction of intermolecular hydrogen bonding [5].

In ionic systems, the presence of ions covalently bound to the polymer chains strongly affects the segmental dynamics by restricting motion near aggregates and creates
an additional segmental process in regions with dispersed ionic groups [6]. In polymer-salt complexes such as poly(propylene oxide)-lithium perchlorate, the addition of salt induces microphase separation into regions of high and low salt content, thereby creating two observable segmental processes [7].

In addition to the scientific aspects, the study of molecular motions is significant by virtue of its relevance to applications. Fundamental understanding of dynamics in polymer systems containing intermolecular bonding is integral to the design of packaging materials, in which the diffusion of molecules or ions is coupled to segmental motion of the host polymer. Organic electronics and optics rely on functional group orientation, which is disrupted by active local processes. Also, control of viscosity and modulus, respectively fundamental to melt and solid-state mechanical properties, is derived from segmental dynamics [8,9].

DRS, with its large accessible frequency and temperature windows, can serve as the primary tool to establish a systematic understanding of intermolecular interactions in polymer systems. Previous studies have indicated that the dynamics of systems with intermolecular bonding are complex, and many issues related to dynamics in systems with strong intermolecular bonding are unresolved. This thesis includes several dielectric studies of these systems, along with results from complementary techniques that assist interpretation, particularly helping to clarify and assign the assorted relaxations that appear in polymers in the presence of strong intermolecular bonds.
1.2 Organization

Within the context of understanding the effect of intermolecular bonding on polymer dynamics, this thesis presents the dielectric behavior of four systems: sulfonated polystyrene (SPS) in the acid form, SPS neutralized by metallic cations, P2VPy with added salt, and P2VPy with added hydrogen-bonding small molecules. In addition to results from DRS, several techniques were used in a complementary role to assist interpretation and enhance the effectiveness of DRS. These techniques include Fourier-transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), small-angle X-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD).

In addition to the motivation and organization, Chapter 1 will provide a brief introduction to DRS theory and the methods used in analyzing experimental results. It will also include background on SPS and ionomers in general, since SPS ionomers are a primary focus of this thesis. Other appropriate background on salt-containing and hydrogen-bonded polymer solutions will be incorporated into Chapters 5 and 6, respectively.

SPS was chosen for the first part of this study because: (1) it is straightforward to synthesize; (2) PS is amorphous; and (3) PS provides a relatively dielectrically-inactive background signal for easy measurement of the dielectrically-active sulfonated groups. Also, the degree of sulfonation can be controlled and the properties of a series of SPS can then be compared with those of PS. The details of sample preparation and characterization techniques are given in Chapter 2.
In order to clearly analyze and interpret the DRS spectra of the ionomers, it is essential to first understand the behavior of unneutralized SPS polymers (SPS-H). The dynamics of SPS-H will be presented in Chapter 3 (published in *Macromolecules* 2006, 39, 1815). SPS-H was synthesized from monodisperse PS at 1 and 7 mol % sulfonation. The dielectric dynamics will be analyzed in the context of data obtained from complementary techniques, in part to connect with previous research on SPS copolymers.

In Chapter 4, the effects of selected neutralizing cations on segmental and local polymer motions will be provided along with the contributions of Maxwell-Wagner-Sillars (MWS) and electrode polarization (published in *Macromolecules* 2007, 40, 991). This chapter is focused on SPS with 7 mol % sulfonation neutralized by exchanging the acid functionality to Na\(^+\), Cs\(^+\) and Zn\(^{2+}\). DRS is the primary tool used to investigate the dynamics, and DMA, SAXS, FTIR and DSC are employed in a complementary role.

Previous investigations of polymer-salt complexes have revealed multiple relaxations and complicated dynamical behavior [10-13], encouraging further study. In Chapter 5, the dynamics of P2VPy - lithium perchlorate complexes will be presented. The interpretation will be complemented by results from FTIR, DSC, WAXD, SAXS, and DMA.

Chapter 6 provides a study of the effect of intermolecular hydrogen bonding on the dynamics of poly(2-vinylpyridine) mixed with low-molecular weight solids that are capable of multiple hydrogen-bonds. Several low-molecular weight materials were chosen to focus on the effect of the number of hydroxyl groups per molecule capable of hydrogen bonding.

Finally, Chapter 7 contains a summary and suggestions for future research.
1.3 Basic Principles of Dielectric Relaxation Spectroscopy

Dielectric relaxation spectroscopy (DRS) involves the interaction of electromagnetic fields with the electric dipoles of materials in the frequency range $10^{-6}$ Hz to $10^{12}$ Hz [14-19]. Macroscopically, when an electric field is applied across a capacitor, positive charge is stored on one plate and negative charge is stored on the other. The capacitance $C_0$ is related to the quantity of charge stored on both plates $Q_0$ and the voltage applied across the plates $V_0$

$$C_0 = \frac{Q_0}{V_0}$$

(1.1)

When material is inserted between the parallel plates, the capacitance increases due to the ability of the material to neutralize the field and allow the plates to store additional charge. The charge on the electrodes increases from $Q_0$ to $Q$ and the capacitance $C_0$ increases to $C$. The increase in $Q$ results from the polarization $P$ induced in the dielectric material by the applied field. The ratio of $C$ to $C_0$ is thus obtained

$$\varepsilon = \frac{Q}{Q_0} = \frac{C}{C_0} = \frac{Q+P}{Q}$$

(1.2)

where $\varepsilon$ is the relative permittivity or the dielectric constant. Since capacitance is also a function of the area $A$ and the distance between the plates $l$, it can be written

$$C = \varepsilon \varepsilon_0 \frac{A}{l}$$

(1.3)

where $\varepsilon_0$ is the vacuum permittivity ($8.85 \times 10^{-12}$ F/m).

From electromagnetic theory, the electric flux density or dielectric displacement $K$ is equivalent to the stored charge on a plate. The dependence of polarization $P$ on the
applied field \( E \) for a particular material placed between the plates is called the dielectric susceptibility \( \chi \), which is equal to \( \varepsilon - 1 \). The complete relationship is:

\[
P = \chi \varepsilon_0 E = K - \varepsilon_0 E
\]

(1.4)

On the molecular level, when an electric field is applied, there is a shift in the charge centers. In the case of electronic polarization, if the center of the electronic charge shifts by an amount \( \delta \), and the total charge is \( e \), the molecule has a dipole moment \( \mu = e\delta \) [20]. The dipole moment is a vector quantity. At small electric fields, the dipole moment of an individual molecule or portion thereof is proportional to the local electric field, \( E_i \). Then the relationship between the macroscopic polarization, microscopic dipole moment, and the number of dipoles per unit volume \( N_m \) is

\[
P = N_m \mu
\]

(1.5)

There are three types of polarization at the molecular level [14-17]:

(a) Electronic polarization, which results from a slight displacement of the center of electrons with respect to the positive nucleus of any atom by the applied field. This polarization type does not relax at the frequencies used in the present study.

(b) Atomic polarization, which occurs when the bonds between atoms are stretched or the arrangement of atomic nuclei in a molecule or lattice, is distorted by an applied field. The magnitude of the contribution to the overall polarization is much smaller than that of electronic polarization. Atomic polarization is easily visualized in ionic compounds, where the applied field acts to displace cations in one direction and anions in the opposite direction, giving rise to a net dipole moment.
(c) Orientational polarization is found in certain molecules having a permanent or induced dipole moment that rotates and aligns opposite the applied field, giving a net polarization that opposes the applied field. The dipolar orientational polarization usually decreases with increasing temperature since the alignment tendency is disturbed by thermal vibration, which is in contrast to electronic and atomic polarization.

1.3.1 Dielectric Relaxations

The discussion of macroscopic and microscopic polarizations in the previous section was done in the context of static electric fields. However, dielectric relaxation spectroscopy utilizes an alternating electric field applied to a sample. Since the phenomenon of dielectric relaxation reflects the retardation in the frequency response of the dipolar groups with applied field, and the orientation of any dipole cannot instantaneously follow the variation of the field, it is convenient to express the frequency response in terms of the complex dielectric permittivity $\varepsilon^*$, which also related to the time-dependent dielectric function $\varepsilon(t)$ [21]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty - \int_0^\infty \frac{d\varepsilon(t)}{dt} \exp(-i\omega t) dt$$  \hspace{1cm} (1.6)$$

where $\omega$ is the angular frequency ($\omega = 2\pi f$). $\varepsilon'(\omega)$ is the real part the permittivity, and is proportional to the energy stored reversibly in the system per period. $\varepsilon''(\omega)$ is the imaginary part (out of phase) portion, and is proportional to the energy dissipated per
period. The limiting dielectric constant at very high frequencies is \( \varepsilon_\infty \), often referred to as the unrelaxed dielectric constant.

The real and imaginary components of \( \varepsilon^* \) are dependent on each other as described by the Kramers-Kronig (KK) relationships [19,21]

\[
\varepsilon'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega') \frac{\omega'}{\omega'^2 - \omega^2} d\omega'
\]  

(1.7)

\[
\varepsilon''(\omega) = \frac{\sigma_0}{\varepsilon_{\text{vac}}} \omega + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon'(\omega') - \omega}{\omega'^2 - \omega^2} d\omega'
\]  

(1.8)

where \( \omega' \) is an integration variable, used to prevent singularities in the integrands, and \( \sigma_0 \) is the dc conductivity. The KK relationships allow determination of the dielectric relaxation strength \( \Delta \varepsilon \) from integration of the dielectric loss, \( \varepsilon'' \). Specifically this is evaluated as the area under the loss peak \( \varepsilon''(\omega) \) or from the step in \( \varepsilon'(\omega) \):

\[
\varepsilon_s - \varepsilon_\infty = \Delta \varepsilon = \frac{2}{\pi} \int_0^\infty \varepsilon''(\omega) d\ln \omega
\]  

(1.9)

\( \varepsilon_s \) is the limiting low frequency or relaxed permittivity.

A commonly-used relationship between the macroscopic \( \Delta \varepsilon \) and the microscopic dipole moment is expressed by Frohlich-Kirkwood theory [18] as

\[
\Delta \varepsilon = \frac{3 \varepsilon_s}{2 \varepsilon_s + \varepsilon_\infty} \frac{4 \pi N_r}{3kT} \left( \frac{\varepsilon_\infty + 2}{3} \right)^2 g_r \mu^2
\]  

(1.10)

where \( N_r \) is the concentration of the repeat units, \( k \) is Boltzmann’s constant, and \( g_r \) is the Kirkwood reduction factor, which takes into account the averaged orientations of dipoles.
1.3.2 Models and Analysis of Dielectric Relaxation Spectra

The basic dielectric relaxation model function is the Debye function (Figure 1.1), for which the loss peak is symmetric with a half width of 1.14 decades [21].

\[ \tau_D \text{ is the Debye relaxation time, related to } \omega_{\text{max}} = \frac{2\pi f_{\text{max}}}{1 + i \omega \tau_D} \] 

\[ \Delta \varepsilon = \varepsilon_S - \varepsilon_{\infty} \]

\[ \varepsilon'' = \log \frac{\varepsilon''}{\varepsilon'} \]

\[ \log \left( \omega / \omega_{\text{max}} \right) \]

**Figure 1.1.** Schematic plot showing \( \varepsilon' \), \( \varepsilon'' \) and \( \Delta \varepsilon \) as a function of normalized frequency for a Debye relaxation process [20].

The Debye function is written

\[ \varepsilon_D^*(\omega) = \varepsilon_{\infty} + \frac{\Delta \varepsilon}{1 + i \omega \tau_D} \]  

\[ (1.11) \]

where \( \tau_D \) is the Debye relaxation time, related to \( \omega_{\text{max}} = 2\pi f_{\text{max}} = 1/\tau_D \).

Dielectric relaxations observed for polymers usually display broadened loss peaks. The shape of the \( \alpha \) relaxation is also typically asymmetric, i.e., exhibiting a high
frequency shoulder. The first modification to the Debye model was the addition of a semi-empirical broadening parameter to obtain the Cole-Cole relation

$$\varepsilon^*_{CC}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega\tau_{CC})^m}$$  \tag{1.12}

where $\tau_{CC}$ is the Cole-Cole relaxation time, and $m$ is the symmetrical broadening parameter (0 < $m$ ≤ 1). Cole and Davidson proposed another semi-empirical modification, based on experimental data for liquids and low molecular glass-forming materials

$$\varepsilon^*_{CD}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{(1 + i\omega\tau_{CD})^n}$$  \tag{1.13}

where $\tau_{CD}$ is the Cole-Davison relaxation time and $n$ is a parameter (0 < $n$ ≤ 1) describing asymmetric broadening for frequencies $\omega > 1/\tau_{CD}$. Later, Havriliak and Negami (HN) introduced a combination of the Cole-Cole and Cole-Davidson models

$$\varepsilon^*_{HN}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{[1 + (i\omega\tau_{HN})^m]^n}$$  \tag{1.14}

where 0 < $m$, $mn$ ≤ 1.

In addition to relaxation peaks, a conductivity contribution to the loss is often observed in the dielectric spectra of polymers at low frequencies and high temperatures. Ideally, conduction creates no contribution to $\varepsilon'$ while $\varepsilon'' = \frac{\sigma_0}{\varepsilon_0\omega}$. In practice, $\varepsilon''$ is proportional to $\omega^{-s}$, where $s$ is a term that characterizes the conduction process ($s$ ≤ 1). Then the complete dielectric spectrum is represented by

$$\varepsilon^*(\omega) = -i\frac{\sigma_0}{\varepsilon_0\omega} + \sum \varepsilon^*_{HN,i}(\omega)$$  \tag{1.15}
Several methods are capable of removing or minimizing dc conduction in dielectric loss spectra via transformation of the dielectric constant: a numerical KK transform $\varepsilon''_{KK}$; a first-order approximation of the KK transform, based on the logarithmic derivative, $\varepsilon''_{der}$; and the dielectric modulus, $M^*$. The numerical KK transform is calculated from [3]

$$\varepsilon''_{KK} = \sum_{k=1}^{4} a_k [\varepsilon'(\omega/2^k) - \varepsilon'(2^k/\omega)]$$

(1.16)

where $a_1 = 0.4453, a_2 = 0.22726, a_3 = -0.11, and a_4 = 0.13458$. The logarithmic derivative is written

$$\varepsilon''_{der} = -\pi \frac{\partial \varepsilon'(\omega)}{2 \frac{\partial \ln \omega}{\partial}}$$

(1.17)

and the dielectric modulus is obtained from [3]

$$M^*(\omega) = M'(\omega) + iM''(\omega) = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + i \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$$

(1.18)

1.4 Background on Ionomers

Ionomers are polymers containing ions covalently attached to the chains, and most of the anions are in a bound state, neutralized partially or completely with cations [22,23]. Ionomers are high-performance materials that display marked improvement over the neat material in electrolytic transport and physical properties. The enhancements in physical properties result primarily from the aggregation of ionic species into clusters [22-26], which act as physical crosslinks. Clusters are typically viewed as roughly spherical aggregates about 3-10 nm in diameter [22]. Hydrocarbon segments attached to
the ionic groups are believed to be immobilized in the corona (the chains surrounding each cluster) [26]. Ionomers can be either amorphous or semi-crystalline based on the chemistry of the hydrocarbon backbone. Several types of ionomers have been utilized for applications such as packaging, coating, adhesives, catalysts, fluid additives, tough molded objects, and ion-exchange membranes in fuel cells [22].

1.4.1 Classification of Ionomers

The various types of ionomers may be classified based on the architectural features of the backbone and the types of ionic groups. A classification of ionomers based on backbone architecture is presented in Figure 1.2.

![Figure 1.2. Classification types of ionomers [24].](image-url)
Monochelics contain a single ion at the end of a polymer chain, for example, polystyrene with a terminal carboxylate anion. Such an ionomer is prepared by anionic polymerization [24]. Telechelics and telechelic stars consist of a single ion at each chain end. The best-known members of the telechelic and telechelic star groups include polyisoprene terminated by carboxylate groups and polyisobutylene stars terminated by sulfonated groups, respectively. Block ionomers include AB diblocks, where one of the segments is nonionic and the other contains an ionic repeat unit, and ABA triblocks, which consist of a nonionic segment B capped at each end by A segments containing ionic groups. Random copolymers are the most common type of ionomer. Others include ionenes, in which the ionic groups are distributed at well-determined spacing along the main chain (the most common ionic groups are quaternary ammoniums), comb ionomers, graft ionomers and dendrimer ionomers [7,22,24]. Dendrimer ionomers are densely-branched polymers that consist of three parts: core, branch cells and ionic terminal groups.

Additionally, ionomers can be classified based on the type of ionic group attached directly to the chains, which can be either anionic or cationic. Anionic ionomers are more common, and usually contains carboxylic, sulfonic, phosphoric or selenonic acids as the pendant group. The less common cationic ionomers have a cationic pendent group such as pyridine, aliphatic amine, or aromatic amine.
1.4.2 Structural Features and Morphology

The smallest ionic arrangement that has a significant impact on intermolecular interactions is a multiplet, which contains 3-10 ion pairs [24]. The size of the multiplet depends on the geometric arrangement of ions, the size of the ion pair, the size of the chain segment covalently attached to the ion, the distance between ion pairs, and the electrostatic energy between ion pairs. At low ion concentration, multiplets may disperse into the bulk and play a relatively minor role in the behavior of the bulk material, or may act as crosslinks and thus influence the bulk behavior. At higher ion concentration, multiplets aggregate into clusters, which act as physical crosslinks and exhibit phase behavior different from the bulk (Figure 1.3).
During the last 30 years there have been a large number of studies of ionomer structure, morphology, and physical properties by techniques such as differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). The following sections will present pertinent findings obtained from these techniques and their relevance to ionomers.

Figure 1.3. Schematic morphological representations of random ionomers at different ion concentration: (a) low ion content, (b) intermediate ion content and (c) high ion content. The shaded areas indicate regions of restricted mobility [22].
1.4.2.1 Glass Transition Temperature

DSC has been used to measure the glass transition temperature (T_g) of ionomers, which is heavily influenced by ion concentration and ionic character. Ionomers with low ion content do not contain restricted mobility regions because there are no aggregates (Figure 1.3), and therefore only a single T_g is expected. At high ion content, two T_g's would be expected because there are a large number of aggregates that create regions of restricted mobility (larger than 5-10 nm), and these domains exhibit T_g behavior different from the bulk [24]. There are only a few cases where DSC can actually detect two T_g's at high ion content, i.e., poly(ethyl acrylate-co-sodium acrylate), sulfonated-ethylene-propylene-ethylene norbonene, n-butyl acrylate-zwitterionomer, and poly(styrene-co-methacrylic acid) [24].

A single T_g, associated with the matrix phase, is most often observed for ionomers with intermediate and high ion content [27-31]. It has been noted that this T_g increases with acid components and degree of neutralization, due to the presence of ionic groups dispersed in the hydrocarbon phase [32]. As an example, the plot of T_g versus ion content of unneutralized and completely neutralized poly(ethyl acrylate-co-methacrylic acid) (P(EA-co-MAA)) with Cs^+ and Ca^{2+} ions is shown in Figure 1.4. T_g of the neutralized samples dramatically increases beginning at ~15 mol % MAA, and is strongly dependent on the type of counterion [33].
1.4.2.2 State of Ionic Species

Fourier-transform infrared spectroscopy (FTIR) is the one of the most straightforward techniques for characterization of the local ionic environment in poly(ethylene-co-methacrylic acid) (P(E-co-MAA)) and sulfonated polystyrene ionomer (SPS) [34-38]. Most spectral bands have been assigned based on calculations of the bond energies or from the relative changes in the position of bands with changes in the degree of neutralization. For example, FTIR investigations by Coleman, Painter, et al have revealed the local structure of partially and completely Zn$^{2+}$ neutralized P(E-co-MAA),

Figure 1.4. Glass transition temperature vs ion content of unneutralized and neutralized P(EA-co-MAA) [24].
containing 26 wt % of methacrylic acid [35]. They reported that the state of Zn$^{2+}$ was impacted by the degree of neutralization, which changed from tetra-coordinated to zinc acid salt structures (Figures 1.5 and 1.6).

**Figure 1.5.** Schematic representation of local structure based on the observed FTIR spectra [35].
The vibration of sulfonated anions (SO$_3^-$) neutralized with different types of cations has been analyzed for SPS [37,38]. The symmetric stretching vibration of the SO$_3^-$ anion appears at ~1040 cm$^{-1}$ and a doublet associated with the antisymmetric stretching vibration appear in dry samples at ~1200 cm$^{-1}$ [37,38]. This doublet is created when the degeneracy of the antisymmetric stretching vibration of the SO$_3^-$ anion is

![Figure 1.6](image-url)
removed by interaction with the cation, and the degree of band splitting is dependent on the field strength of the cation [37-39].

1.4.2.3 Ionic Clusters and Phase Separation

Ionic clusters have been directly observed by transmission electron microscopy (TEM) [40-45]. The diversity of cluster sizes and shapes are dependent on cation type, degree of neutralization and chemical structure of the polymer backbone. Figures 1.7 and 1.8 show TEM images of poly(butadiene-co-methacrylic acid), neutralized 100 % with Na⁺ [45], and of SPS with 4 mol % sulfonation, neutralized with Zn²⁺ [42], respectively. Although TEM is a powerful tool for studying the ionomer morphology because of strong contrast between the clusters and the hydrocarbon regions, the small size of ionic clusters makes it difficult to obtain clear images. It is also uncertain how the methods involved in sample preparation affect the observed features. Handlin et al [40] pointed out that features observed using TEM may arise from phase gain artifacts, due to residual salts or defocusing.
Several models of ionomer morphology have been proposed based primarily on data obtained by SAXS [23-27,32,44,46-59]. These models include the hard-sphere model [46-48], the core-shell model [44,49] and the Eisenberg-Hird-Moore (EHM), or
restricted mobility, model [26]. A modified hard-sphere model, which accounts for aggregates surrounded by and attached to the hydrocarbon matrix, provided a good fit of experimental data, as reported by Yarusso and Cooper [48]. The restricted mobility EHM model was built on the Yarusso-Cooper model to account for both scattering and mechanical data [59]. The formation of ionic aggregates is driven by electrostatic forces and the total number of ion pairs per aggregate is limited by the size of the ion pair and the steric effects of the polymer chains surrounding the multiplet as corona (Figure 1.9). The formation of aggregates is also affected by the dielectric constant of the polymer backbone: when the dielectric constant of the polymer is high, the ions are solvated, and no multiplets are formed [22].

![Image of restricted mobility model](image_url)

**Figure 1.9.** Corona structure of the restricted mobility model [58].

Results from SAXS have demonstrated that, for Na\(^+\) and Zn\(^{2+}\) neutralized SPS, the scattering intensity \(I_q\) increases and the peak maximum moves to higher scattering...
vector $q$ with increasing degree of neutralization (see Figure 1.10 for SPS-Na [32]). This is due to an increase in the number of scattering sites and a reduction in the mean intercluster spacing, calculated from $d = 2\pi/q$ [32,50].

Figure 1.10. SAXS profiles of SPS-Na ionomers as a function of neutralization [32].

The temperature dependence of the scattering peak maxima of 7.6 mol % SPS neutralized by Mn$^{2+}$ cations has been reported by Galambos et al [27]. They found that a scattering maximum is absent below 165 °C, but above this temperature a peak developed (Figure 1.11). They explained that no microphase separation of ionic clusters occurs in the cast ionomers, and the ionic aggregates are created upon heating above 165 °C. It is commonly observed that increasing temperature above a certain temperature allows reorganization of the chains and the formation of ionic aggregates [27].
Previous SAXS studies of ionomers have reported some apparently contradictory results. This has arisen primarily because of different methods of sample preparation and sample thermal history [27,32,48,56,57]. For example, Weiss and Leflar [32] found that thermal history strongly affects the scattering intensity of melt-pressed SPS-Zn: increasing thermal aging time reduces peak scattering intensity without changing the location of the peak maximum. This indicates a decrease in the concentration of ionic clusters. In contrast to SPS-Zn, increasing the annealing temperature for SPS-Na results

\[\text{Figure 1.11. SAXS profiles of 7.6 mol \% SPS-Mn as a function of temperature [27].}\]
in the peak maximum moving to smaller $q$ together with an increase in scattering intensity. A similar result was also reported by Yarussso and Cooper, where the “ionomer peak” was retained for annealed SPS-Na [48]. On the other hand, Grady et al found that a compression-molded SPS-Na sample resulted in the low-angle upturn but no visible ionomer peak, where the low-angle upturn has been associated with long-range inhomogeneity of the metal ions [57]. Also, Galambos et al found that a solution-cast sample of SPS-Mn did not exhibit any ionomer scattering peak until heating the sample above $T_g$ [27].

### 1.4.2.4 Mechanical Relaxations

Many investigations of ionic aggregate structure have utilized dynamic mechanical analysis (DMA) [28, 29, 60-69]. Sulfonated polystyrene neutralized with sodium (SPS-Na) is one case where the dynamic mechanical properties have been studied extensively [28, 62-64]. Hara et al [62] and Hird and Eisenberg [63] both observed two loss peaks for SPS-Na containing more than 3.5 mol % Na$^+$ (Figure 1.12). They concluded that the lower-temperature segmental loss peak arises from a phase containing only dispersed ionic multiplets, whereas the higher-temperature peak corresponds to a transition from a phase containing ionic aggregates. Additionally, Weiss et al [28] obtained two loss peaks for SPS-Na containing 2 to 6 mol % Na$^+$ (Figure 1.13), which were attributed to the segmental motion of the matrix phase and the motion of chains associated with the ionic clusters. The higher-temperature peak was found to shift to higher temperature with an increase in Na$^+$ content.
Figure 1.12. (a) Mechanical storage modulus and (b) mechanical loss tangent of SPS-Na at various Na⁺ content [62].

Figure 1.13. (a) Mechanical storage and (b) mechanical loss modulus as a function of temperature for PS and three fractions of SPS-Na, obtained at 1 Hz [28].
Other styrene-based ionomers such as poly(styrene-co-methacrylic acid) [24,44,64-67], poly(styrene-co-acrylic acid) [68], and carboxylated polystyrene [69] also display two transitions when ion content is above 4 mol %. The two transitions observed at low and high temperature by DMA are typically understood as the transitions associated with the glass transition of the matrix and the glass transition of the cluster phase.

Hara et al [62,70] found that SPS sulfonated at 4.1 mol % and neutralized by Ca$^{2+}$ displays an extended rubbery plateau region relative to ionomers neutralized with K$^+$ and Cs$^+$. This is due to the divalent cations, which have higher field strength than monovalent cations; in addition, the trend in the magnitude of storage modulus was found to be Zn$^{2+} >$ Ca$^{2+}$ [71]. The temperature at which the rubbery plateau region decreases also indicates the onset of ion hopping [63,67]. Ion hopping corresponds to the long-range migration of ion pairs between clusters at high temperature. It has been studied in SPS-Na by Hird and Eisenberg by considering the temperature dependence of the storage modulus [63]. The onset of ion hopping at a given frequency is usually taken as the intersection of linear segments in the storage modulus plateau.

1.4.3 Dielectric Relaxations of Ionomers

Despite the power of DRS in understanding polymer dynamics, it has only been used in a few cases to study ionomers. Two relaxations have been observed for the acid form with 13 mol % acid content (Figure 1.14) [6,72-75]. The process labeled $\gamma$ has been assigned to local molecular motion of short segments in the amorphous region that
contain acidic species. The relaxation labeled $\beta'$ was assigned to segmental motion in the amorphous region, restricted by the intermolecular bonds between acid dimers. In the 13 mol % ionomer form neutralized by 20 % Na$^+$ and 60 % Zn$^{2+}$ cations, the $\beta'$ relaxation shifts to higher temperatures. This shift is ascribed to the formation of ionic aggregates acting as physical crosslinks [6]. However, for the same ionomer neutralized with 60 % Na$^+$, three relaxations were observed, corresponding to local motion ($\gamma$), segmental motion of the amorphous region containing well-dispersed cationic groups ($\beta$), and segmental motion of amorphous chains closely connected to the ionic aggregates [6].

Figure 1.14. Dielectric loss as a function of temperature of P(E-co-MA) ionomers, neutralized with Na$^+$ and Zn$^+$ at 1 Hz [6].

A dielectric study of P(S-co-MA), containing 2 to 9 mol % sodium was conducted by Hodge and Eisenberg [75]. They observed two loss tangent peaks after subtracting dc conductivity, and assigned the lower-temperature peak to the segmental motion of regions with lower salt content and assigned the higher-temperature peak to the
segmental relaxation of regions with higher salt content. The two loss tangent peaks shift to higher temperature with increasing ion content, as seen in Figure 1.15. The maximum of the lower temperature peak is unchanged at ion contents greater than 5 mol %, whereas the maxima of the higher temperature peak increase steadily with ion content.

Figure 1.15. Loss tangents as a function of temperature at $10^2$ Hz for P(S-co-MA) at various Na$^+$ content. The sodium content is indicated in the figures [76].
1.5 References

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Chapter 2
Experimental

2.1 Materials and Sample Preparation

2.1.1 Sulfonation of Polystyrene

Narrow molecular weight distribution polystyrene (PS) having $M_w = 119600$ and $M_n/M_w = 1.04$, purchased from Polymer Source, was sulfonated with acetyl sulfate according to a procedure widely reported in the literature to produce random SPS copolymers [1,2]. Acetyl sulfate was prepared by mixing sulfuric acid (99.9%) with acetyl anhydride (99.5%) in an ice bath under flowing N$_2$ gas. The PS was dissolved in 1,2-dichloroethane and heated to 50 °C under an N$_2$ purge for 30 min. Acetyl sulfate solution was added while stirring. The reaction (Figure 2.1) was maintained at 50 °C for 5 h. The reaction was terminated by adding 2-propanol, and the polymer precipitated into 2-propanol. The sulfonated polymer (SPS-H) was isolated by pouring the precipitate into a large volume of boiling distilled water, followed by washing several times with distilled water and methanol. The product was filtered and dried under vacuum at 70 °C for several days.
2.1.2 Alkylation of Sulfonated Polystyrene

The \(-\text{OH}\) groups of unneutralized SPS-H were converted to \(-\text{OCH}_3\), yielding methyl-sulfonated PS (SPS7CH₃), by adding trialkyl phosphate (in 1:1 molar ratio) to SPS7H solution, which was dried by azeotropic distillation using benzene. The reaction was stirred at room temperature for 24 h (Figure 2.2) [3]. The reaction was terminated and the product precipitated by adding methanol and isolated by pouring in boiling water and then washed with cold water and methanol. The SPS7CH₃ was dried and maintained under vacuum at 70 °C for at least 48 h before use.

\[
-(\text{CH}_2-\text{CH})_n + \text{CH}_3\text{C-OSO}_3\text{H} \xrightarrow{\text{1,2-dichloroethane}} \text{50°C, ROH, 5 hrs} \rightarrow -(\text{CH}_2-\text{CH})_{x'}-(\text{CH}_2-\text{CH})_{y'} + \text{CH}_3\text{COOH}
\]

Figure 2.1. Schematic illustration of the sulfonation of polystyrene.

2.1.2 Alkylation of Sulfonated Polystyrene

\[
-(\text{CH}_2-\text{CH})_x-(\text{CH}_2-\text{CH})_y + (\text{CH}_3\text{O})_3\text{P} \xrightarrow{\text{CH}_2\text{Cl}_2} \text{Tr, 24 hrs} \rightarrow -(\text{CH}_2-\text{CH})_{x'}-(\text{CH}_2-\text{CH})_{y'} + (\text{CH}_3\text{O})_2\text{P(O)H}
\]

Figure 2.2. Schematic illustration of the alkylation of sulfonic acid polystyrene.
2.1.3 Neutralization of Sulfonated Polystyrene

Neutralization was accomplished as described in the literature (Figure 2.3) [2]. The acid form of the appropriate SPS copolymer (SPS-H) was dissolved in chloroform. A measured amount of sodium hydroxide, zinc acetate or cesium hydroxide was dissolved in methanol/water (2:1) and added to the SPS-H solution with stirring for 5 h at 60 °C under flowing N₂ gas. The neutralized sulfonated polystyrenes (SPS-M) were precipitated with ethanol, followed by washing with hot water and methanol, filtered, and dried under vacuum at 100 °C for 48 h before sample preparation.

\[
\text{-(CH}_2\text{-CH)}_x\text{-(CH}_2\text{-CH)}_y + \text{MOH} \xrightarrow{5 \text{ hrs}} \text{-(CH}_2\text{-CH)}_x\text{-(CH}_2\text{-CH)}_y + \text{H}_2\text{O}
\]

Figure 2.3. Schematic illustration of the neutralization of sulfonic acid polystyrene.

2.1.4 Degree of Sulfonation

The sulfonation level of SPS-H polymers was determined by titration with a standard 0.05 M NaOH solution in methanol. The normality of the standard solution was determined by 0.05 M p-toluenesulfonic acid in methanol using a phenolphthalein indicator. The SPS samples were dissolved in a 9:1 THF: methanol mixture. The degree of sulfonation y is the molar percentage of styrene repeating units properly sulfonated (SPSyH) (Figure 2.1). Sulfonation levels of the two concentrations studied were 1.1 and
6.8 mol%. The unneutralized versions of these polymers are referred to as SPS1H and SPS7H, respectively.

2.1.5 Degree of Neutralization

Degrees of neutralization were estimated by measuring the remaining acid content of the materials via a titration method, as described in section 2.1.4. The percent neutralization is presented in Table 2.1. The degrees of neutralization of all ionomers are ca. ~ 90 %. The neutralized versions are referred to as SPS1Na, SPS7Na, SPS7Cs and SPS7Zn.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfonation level (mol%)</th>
<th>Degree of Neutralization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS7H</td>
<td>6.8</td>
<td>0</td>
</tr>
<tr>
<td>SPS1H</td>
<td>1.1</td>
<td>0</td>
</tr>
<tr>
<td>SPS1Na</td>
<td>1.1</td>
<td>90</td>
</tr>
<tr>
<td>SPS7Na</td>
<td>6.8</td>
<td>86</td>
</tr>
<tr>
<td>SPS7Cs</td>
<td>6.8</td>
<td>86</td>
</tr>
<tr>
<td>SPS7Zn</td>
<td>6.8</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 2.1. Sulfonation levels and degree of neutralization of SPS-H and SPS-M.
2.1.6 Water Content

Water contents of SPS copolymer and SPS ionomers were measured using a coulometric Karl Fischer titration method (KF titration). Hydranal CG and Hydranal A were used as catholyte and anolyte reagents. The samples were dissolved in chloroform and injected into the large cell compartment; iodine continues to be generated by the titrator until an endpoint is determined (see Figure 2.4 for the Bunsen reaction [4]). Modern microprocessor-controlled coulometric titrators calculate the amount of iodine generated based on the total current required to reach an endpoint. The water contents of SPS-H and SPS-M, before and after DRS experiments was found to be less than 0.3 wt % as shown in Table 2.2. The water content of SPS7Zn was not measure since it was not soluble in chloroform. Consistently, Weiss et al [5] have reported water absorption at room temperature after 24 days for 5.2 mol % sulfonation PS to be 0.4 wt %. This suggests that it is difficult for water to absorb in to SPS copolymers and ionomers with low degree of sulfonation.

\[
2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}
\]

Figure 2.4. The Bunsen reaction [4].
2.1.7 Poly(2-vinylpyridine) and Lithium Perchlorate Mixtures

Poly(2-vinylpyridine) (P2VPy) with Mw ~ 100,000 was purchased from Scientific Polymer Products. Lithium Perchlorate (LiClO₄) was obtained from Aldrich and used without purification. P2VPy - LiClO₄ mixtures were prepared by mixing (with stirring) of P2VPy in methanol with 0.1, 0.5, 1, 5 and 10 mol % of LiClO₄ in methanol, subsequently referred to as P2VPy - 0.1Li, P2VPy - 0.5Li, P2VPy - 1Li, P2VPy - 5Li and P2VPy - 10Li respectively. The mixing was conducted at 50 °C for 2 h and stirring was continued at room temperature for 24 h. Sample films for DSC, WAXD, DMA, SAXS and DRS measurements were prepared by solution casting from methanol: solvent was evaporated at room temperature for 48 h, followed by gradually heated to 120 °C under vacuum, and maintained at 120 °C for 24 h to remove solvent and water.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before DRS</td>
</tr>
<tr>
<td>SPS1H</td>
<td>0.24</td>
</tr>
<tr>
<td>SPS7H</td>
<td>0.22</td>
</tr>
<tr>
<td>SPS1Na</td>
<td>0.22</td>
</tr>
<tr>
<td>SPS7Na</td>
<td>0.27</td>
</tr>
<tr>
<td>SPS7Cs</td>
<td>0.28</td>
</tr>
</tbody>
</table>
2.1.8 P2VPy and Low Molecular Weight Phenolic Molecule Mixtures

Bis (4-hydroxyphenyl) methane (BPM), 2,6 Dihydroxynaphthalene (DHN), and 4-Ethyphenol (EPh) were obtained from Aldrich. 2,2-Methylenebis[6-(2-hydroxy-5-methylbenzyl)-p-cresol] (MHM) and 2,3,3,4,4,5-Hexahydroxybenzophenone (HDP) were purchased from TCI America. The structures of these hydroxyl-containing molecules are provided in Figure 2.5 and their glass transitions, melting temperatures and boiling points are provided in Table 2.3. Tgs in Table 2.3 were estimated from \( T_g = T_m / 1.3 \) [6], since \( T_g \) could not be determined directly. P2VPy/BPM, P2VPy/DHN, and P2VPy/EPh mixtures were prepared by mixing (with stirring) of P2VPy in methanol with 10, 30 and 50 mol% of BPM, DHN, and EPh in methanol for 24 h. P2VPy/MHM and P2VPy/HDP mixtures were prepared by mixing P2VPy with MHM and HDP in DMF while stirring. All polymer mixtures were prepared in a film form by evaporating the respective solvent. Films were heated to 120 °C under vacuum for 24 h to remove solvent and water.
Figure 2.5. Chemical structures of P2VPy, EPh, BPM, DHN, MHM and HDP.
Table 2.3. Estimated glass transitions, experimental melting points and literature values for boiling points of EPh, BPM, DHN, MHM, and HDP.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(_g) (°C)</th>
<th>T(_m) (°C)</th>
<th>T(_b) (°C) [Source]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2VPy</td>
<td>107</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>EPh</td>
<td>-28</td>
<td>45</td>
<td>218 [Aldrich]</td>
</tr>
<tr>
<td>BPM</td>
<td>62</td>
<td>162</td>
<td>220 [Aldrich]</td>
</tr>
<tr>
<td>DHN</td>
<td>110</td>
<td>225</td>
<td>decomposes [Aldrich]</td>
</tr>
<tr>
<td>MHM</td>
<td>74</td>
<td>178</td>
<td>259 [TCI America]</td>
</tr>
<tr>
<td>HDP</td>
<td>28</td>
<td>115</td>
<td>290 [TCI America]</td>
</tr>
</tbody>
</table>

2.2 Characterization Techniques

2.2.1 Dielectric Relaxation Spectroscopy

Dielectric relaxation spectra were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency domain from 0.01 Hz - 1 MHz. Temperature stability was controlled to ±0.2 °C. For SPS copolymers and ionomers, the samples were heated from 30 to 220 °C. For P2VPy - LiClO\(_4\) and P2VPy mixtures, the samples were heated from -40 to 220 °C and -60 to 190 °C respectively. All sample films were 0.1-0.3 mm thick. Sample surfaces were sputtered with gold, covered by a silver sheet and tightly sandwiched between electrodes of 2 cm diameter.
Data Processing

The relaxation time \( \tau_{\text{max}} \) \( (\tau_{\text{max}} = 1/2\pi f_{\text{max}}) \) and dielectric relaxation strength \( \Delta \varepsilon \) were obtained by fitting the isothermal dielectric loss \( \varepsilon''(f) \) curves with the Havriliak-Negami (HN) function. The sum of multiple HN functions and a dc loss contribution were generally used to fit the experimental loss curves [7]:

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty - i\frac{\sigma_0}{\varepsilon_\infty \omega^n} + \sum \frac{\Delta \varepsilon}{[1 + (i\tau_{\text{HN}} \omega)^m]^n} \quad (2.1)
\]

The dielectric loss \( \varepsilon'' \) was also obtained by transforming the dielectric constant \( \varepsilon' \) via a numerical version of the Kramers-Kronig (KK) transform as described in Chapter 1, section 1.3.1. \( \tau_{\text{max}} \) and \( \Delta \varepsilon \) of the segmental \( \alpha \) processes of P2VPy - LiClO\(_4\) complexes and P2VPy/HDP mixtures were conducted by fitting the isothermal \( \varepsilon''_{\text{KK}} \) curves with Eq. 2.1.

2.2.2 Differential Scanning Calorimetry

Glass transition temperatures \( (T_g) \) were determined using a TA Instruments Q-100 DSC. Temperature was calibrated using an indium standard. All samples, including SPS copolymers, SPS ionomers, P2VPy - LiClO\(_4\) mixtures and P2VPy solutions were in film form, and weighed from 8-10 mg. Samples were first heated from 20 °C to 140 °C at a heating rate of 10 °C/min, held for 5 min, and then cooled at 40 °C/min to 20 °C. After holding for 3 min, samples were reheated to 220 °C at a rate of 10 °C/min. This procedure was used with all samples with an exception of P2VPy/EPh mixtures, the first heating
from 20 °C to 120 °C and the last heating from 0 °C to 150 °C. Results shown in this thesis are taken from the last step.

### 2.2.3 Fourier Transform Infrared Spectroscopy

Infrared spectra were acquired using a Bio-Rad FTS-6 spectrometer, signal averaging 128 scans at a resolution of 2 cm\(^{-1}\). Sample solutions of SPS copolymers, SPS ionomers, P2VPy - LiClO\(_4\) complexes and P2VPy mixtures were deposited on KBr windows and the solvent evaporated at room temperature, followed by gradually heating to 120 °C, and then maintaining at 120 °C under vacuum for 24 h.

### 2.2.4 Dynamic Mechanical Analysis

Dynamic mechanical properties in tensile mode were acquired using a TA Q-800 DMA, at a frequency of 1 Hz. The samples were heated from 50 to 200 °C for SPS copolymers, from 50 to 300 °C for SPS ionomers and from 50 to 250 °C for P2VPy - LiClO\(_4\) and P2VPy/10HDP mixtures with a heating rate of 5 °C/min. The storage (E') and loss moduli (E'\(^\prime\)) were measured as a function of temperature for rectangular films (18 mm × 5 mm × 0.1-0.3 mm).
2.2.5 Small-Angle X-ray Scattering

SAXS profiles for SPS copolymers, SPS ionomers, P2VPy - LiClO₄ complexes and P2VPy mixtures were collected using a two dimensional detector, and the scattering vector was calibrated with silver behenate. A parallel ionization detector was placed in front of the samples to record the incident and transmitted intensities. The sample to detector distance was 1.5 m. Data were acquired for 2 h and azimuthally averaged to yield a one dimensional profile of intensity $I(q)$ vs scattering vector $q$ ($q = (4\pi/\lambda)\sin\theta$), where $\lambda$ is the X-ray wavelength and $2\theta$ is the scattering angle). A mean interdomain spacing was calculated from $d = 2\pi/q$.

2.2.6 Wide-Angle X-ray Diffraction

WAXD pattern were acquired using a Scintag Pad V diffractometer, operated with CuKα radiation ($\lambda = 1.54184$ Å) at 35 kV and 30 mA. The sample films were scanned continuously at a scanning rate of 2.5 °/min and the 2θ range from 5 to 40° (WAXD results of SPS copolymers, SPS ionomers were mentioned but not shown here). The diffraction peaks of P2VPy - LiClO₄ were deconvoluted with PeakFit software, using a linear baseline and adjustable-width Gaussian peaks [8]. The $d$ spacing was estimated from the peak maxima of amorphous halos using the Bragg relation [9].
2.3 References

1. Makowski, H.S.; Lundberg, R.D; Singhal, G. *US Pat.* 3870841, **1975**.


Chapter 3

Dynamics of Sulfonated Polystyrene Copolymers Using Broadband Dielectric Spectroscopy

In this chapter, the dynamics of acid and methylated precursors to sulfonated polystyrene (SPS) ionomers are examined. DRS is used as the primary experimental tool with assistance from DMA, FTIR and DSC. As described in Chapter 1, it is well known that SPS ionomers phase separate with the formation of ionic clusters, however the SPS-H copolymer precursors are somewhat less well understood. This is at least partly due to the observed immiscibility of PS blends with SPS-H with acid contents as low as 1.7 mol% [1], and the possibility of compositional heterogeneity arising from the sulfonation reaction. Previous investigations of neat SPS-H copolymers have examined the possibility of phase separation by SAXS [2-4], TEM [5] and DMA [3,6]. No phase separation was detected with SAXS and TEM, although the presence of a second loss peak in DMA spectra lead to the proposal that phase separation can occurs in SPS-H copolymers [3]. However, for polyisobutylene and polybutadiene transient networks containing a small mole fraction of hydrogen-bonded urazole stickers [7-9], and hydrogen-bonded supramolecular assemblies [10], a relaxation at temperatures higher than the $\alpha$ process has been observed via DRS, but rather than phase separation, this process was assigned to the relaxation of binary hydrogen-bonded networks.
3.1 Glass Transition Behavior

Thermograms of PS, the two SPS-H copolymers and SPS-CH$_3$ are displayed in Figure 3.1. One $T_g$ is observed for all copolymers. At very low degrees of sulfonation (SPS1H), $T_g$ is not distinguishable from that of neat PS. The $T_g$ of SPS7H is approximately the same as SPS7CH$_3$ and slightly higher than SPS1H and PS [3], consistent with increased steric hindrance resulting from the addition of sulfonate groups.

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**Figure 3.1.** DSC Thermograms of PS, SPS1H, SPS7H, and SPS7CH$_3$. 

---
3.2 State of Ionic Species

FTIR spectroscopy is used to confirm the general structure of the synthesized SPS polymers and investigate the state of the sulfonic acid species. Figure 3.2 shows a portion of the spectrum of neat PS together with those of SPS1H, SPS7H and SPS7CH₃. The arrows identify the absorbance bands arising from the sulfonated groups. The peaks at 1370 and 1180 cm⁻¹ have been assigned respectively to antisymmetric and symmetric stretching vibrations of the sulfur-oxygen having double-bond character (O=S=O) [11-13]. The band at 907 cm⁻¹ has been assigned to the stretching vibration of the SO having single-bond character (S-O) [11-13]. The peaks at 1100 cm⁻¹ and 1127 cm⁻¹ in the SPS7H spectra correspond to the in-plane skeletal vibration of the benzene ring substituted by SO₃H and SO₃⁻, respectively [11-13].
In order to aid in interpretation of DRS spectra, the state of the sulfonated species was investigated as a function of temperature. The integrated areas of the bands of interest were deconvoluted and the areas calculated with PeakFit® software, using a linear baseline and adjustable-width Gaussian peaks. The absorbance of the peak at 1100 cm\(^{-1}\) decreases with increasing temperature (see Figure 3.3), whereas that of the 1127 cm\(^{-1}\) absorption rapidly increases at temperatures above 160 °C. This indicates that additional protons dissociate at high temperatures, resulting in additional SO\(_3^-\) anions. Similarly, the absorbance at 1095 cm\(^{-1}\) in the spectrum of SPS7CH\(_3\) is assigned to an in-plane bending vibration of aromatic rings with SO\(_3\)CH\(_3\) substitution (see Figure 3.2). An FTIR temperature study of this copolymer (not shown) reveals that there is no significant
change in the absorbance of the 1095 cm$^{-1}$ band with temperature, in keeping with previous interpretations.

Figure 3.3. (a) FT-IR absorbance spectra of SPS7H at selected temperatures from 40 to 250 $^\circ$C and (b) comparison of the integrated intensity of the free anion band at 1127 cm$^{-1}$ and the bound anion band at 1100 cm$^{-1}$. Error bars represent the 95% confidence intervals calculated from the fitting program.
3.3 Dynamic Mechanical Analysis

Storage and loss moduli for the polymers under investigation are displayed in Figure 3.4. Consistent with the DSC observations, the mechanical $\alpha$ relaxation shifts slightly to higher temperature with increasing sulfonation. The extended rubbery plateau (Figure 3.4a) observed for SPS1H and SPS7H, in contrast with PS and SPS7CH$_3$, demonstrates the importance of H-bonding on the mechanical properties above $T_g$ for SPS-H systems [3]. An increase in the plateau modulus for SPS7H is due to the increased number of reversible H-bonding contacts [14]. The importance of H-bonds above $T_g$ is further supported by the significant reduction in the length of the rubbery plateau for SPS7CH$_3$, where the possibility for hydrogen bonding has been mostly removed. Finally, no other transitions are observed for either SPS1H or SPS7H, and hence there is no indication of significant phase separation in these copolymers.
Figure 3.4. (a) Storage $E'$ and (b) loss modulus $E''$ vs temperature for PS, SPS1H, SPS7H, and SPS7CH$_3$ at 1 Hz.
3.4 Dielectric Relaxation Spectroscopy

3.4.1 Segmental $\alpha$ Process

The relaxation times of the segmental $\alpha$ process ($\tau_\alpha$) are obtained from the maxima in $\varepsilon''$ after subtracting the contribution from dc conductivity. The relaxation times of PS and the SPS copolymers are well fit by the Vogel-Fulcher-Tammann (VFT) [15]:

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$  \hspace{1cm} (3.1)

where $\tau_0$ is sometimes associated with vibration lifetimes [16], B is related to the apparent activation energy ($B = \frac{E_a(1 - T_0 / T)^2}{R}$) [15], and $T_0$ is the Vogel temperature below which segments become immobile. $\tau_0$ is fixed at $10^{-14}$ s to increase fitting accuracy [17]. VFT plots for PS and SPS copolymers are shown in Figure 3.5a. The fitted values for B and $T_0$ are provided in Table 3.1. The dynamic glass transition temperature ($T_g^{\text{DRS}}$) can be determined from [17]:

$$T_g^{\text{DRS}} = T_{\text{ref}} = \frac{B}{\ln(1/\tau_0)} + T_0$$  \hspace{1cm} (3.2)

where $T_{\text{ref}}$ is defined here as the temperature at which the segmental relaxation time is 1 s ($\tau_{\text{max}} = 1$ s). The system cooperativity, correlated with the degree of intermolecular coupling, can be characterized by determining the fragility. Fragility $F$ is defined as [18]:
\[ F = \frac{d \log(\tau_{\text{max}})}{d(T_{\text{ref}}/T)} \bigg|_{T_0}^{T_{\text{ref}}} = \frac{B / T_{\text{ref}}}{\ln(10)(1 - T_0 / T_{\text{ref}})^2} \] (3.3)

**Figure 3.5.** Relaxation times of the \( \alpha \) process obtained from \( \varepsilon'' \) data as a function of temperature for PS, SPS1H, SPS7H, and SPS7CH\(_3\): (a) VFT and (b) fragility plots. Solid lines indicate fits with Eq.3.1 and 3.3, with \( T_{\text{ref}} = T_{g}^{\text{DRS}} \), defined in Table 3.1.
It was anticipated that hydrogen bonding would increase the fragility of the copolymers compared to neat PS, but this is not the case (see Figure 3.5b). Rather, neat PS is a relatively fragile polymer (F ≅ 78) due to the bulky side groups enhancing intermolecular cooperativity [17], and the addition of a relatively small number of hydrogen bonds does not increase the degree of the intermolecular coupling above that of PS. Previous studies point out that in high-fragility polymers, the addition of hydrogen bonding does not have a significant impact on intermolecular cooperativity [19-20].

The $\varepsilon''_{\text{KK}}$ spectra of SPS1H and SPS7H reveal two additional relaxation processes above the segmental relaxation (see Figure 3.6 for SPS7H spectra, those for SPS1H are similar and not shown), which are absent in the spectra of PS and SPS7CH$_3$. Since the former copolymers are single phase materials, Maxwell-Wagner-Sillars interfacial polarization can be ruled out as the origin of these processes. Vinyl homopolymers cannot be intrinsic type-A chains and hence do not exhibit a normal mode relaxation [21]. Random head-to-tail copolymers could exhibit a small dipole moment along the chain

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g^{\text{DSC}}$ ($^\circ$C)</th>
<th>$T_g^{\text{DRS}}$ ($^\circ$C)</th>
<th>VFT parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>105</td>
<td>101</td>
<td>0.186 34</td>
</tr>
<tr>
<td>SPS1H</td>
<td>106</td>
<td>109</td>
<td>0.198 38</td>
</tr>
<tr>
<td>SPS7H</td>
<td>110</td>
<td>109</td>
<td>0.207 35</td>
</tr>
<tr>
<td>SPS7CH$_3$</td>
<td>109</td>
<td>109</td>
<td>0.214 32</td>
</tr>
</tbody>
</table>

**Table 3.1.** $T_g$s and VFT Fit Parameters for PS, SPS1H, SPS7H, and SPS7CH$_3$. 
direction, but at such low comonomer concentrations it is rather unlikely that a normal mode process for SPS1H and SPS7H would be observable.

Figure 3.6. The $\varepsilon''_{KK}$ spectra of SPS7H vs frequency at selected temperatures, indicating the segmental ($\alpha$), H-bond association/disassociation ($\alpha^*$), and electrode polarization ($\alpha_{EP}$) processes.

3.4.2 Electrode Polarization: $\alpha_{EP}$ Process

The highest temperature and lowest frequency relaxation in the loss spectra of SPS1H and SPS7H (for SPS7H in Figure 3.6, see data at $T = 170$ and 220 °C) is attributed to electrode polarization (EP), the phenomenon where mobile ions accumulate at electrode interfaces and act as a large capacitance in series with the sample. The very
large concurrent increase in dielectric constant $\varepsilon'$ at low frequencies (Figure 3.7, for SPS7H) alongside the extremely high losses in $\varepsilon''$ supports this assignment.

\[ \tau_{EP} = \frac{\varepsilon_\infty \varepsilon_0 \ell}{\sigma_0 2 L_D} \]  

\textbf{Figure 3.7.} Frequency dependence of the dielectric constant of SPS7H from 170 to 220 $^\circ$C.

It has been proposed that the $\alpha_{EP}$ relaxation times can be determined to a first approximation from [22]:

where $\varepsilon_\infty$ is the high frequency dielectric permittivity, $\sigma_0$ the (dc) conductivity obtained from the low frequency plateau of the real part of the measured conductivity versus frequency, $\ell$ the sample thickness and $L_D$ the Debye length. The Debye length is the
distance an unpaired counterion must travel to achieve electrostatic neutrality and is inversely proportional to the conductivity. For SPS7H at 190 °C, for example, (where $\sigma_0 = 4.6 \times 10^{-10}$ S-cm$^{-1}$, $\varepsilon_\infty = 6.5$ and $\tau_{EP} = 1.8 \times 10^{-1}$ Hz), $\ell/L_D$ was estimated to be $\sim 270$, implying $L_D \sim 1.4 \mu$m. $L_D$ was calculated to be near $1 \mu$m at all other temperatures. This value is on the same order (ca. $\sim 1 \mu$m) as determined previously for another poorly conducting polymer system [23]. For more highly conducting systems ($>10^{-5}$ S-cm$^{-1}$), such as polyelectrolyte solutions, the Debye length is on the order of 5-10 nm [24].

### 3.4.3 $\alpha^*$ Process

The process referred to here as $\alpha^*$, detected in the $\varepsilon''_{KK}$ spectra of SPS1H and SPS7H, is located between the $\alpha$ and $\alpha_{EP}$ relaxations. It is proposed that this process has an origin comparable to what has been referred to previously as a ‘chemical relaxation’, specifically the association and dissociation of a transient hydrogen bonded sticker [7-10]. In general, the overall relaxation time of such processes has been shown to exhibit a contribution from ‘chemical relaxation’ (sticker association/dissociation) and dipole reorientation processes [8].

The relaxation map for SPS7H is presented in Figure 3.8. The $\alpha$ relaxation should follow a VFT dependency as noted previously, whereas $\alpha^*$ relaxation times are more Arrhenius-like over the temperature range of the data. This supports the assignment of the $\alpha^*$ relaxation, since H-bond association and dissociation should follow Arrhenius
behavior [8]. The activation energy of the $\alpha^*$ process of SPS7H ($E_a \cong 240$ kJ/mol) is about three times higher than that for SPS1H (~75 kJ/mol) [9-10].

Figure 3.8. Temperature dependence of the relaxation times of the $\alpha$, $\alpha^*$, and $\alpha_{EP}$ processes for SPS7H (the former were obtained from $\varepsilon''$ data and the latter two from $\varepsilon''_{KK}$ data). The dotted line through the $\alpha^*$ data represents an Arrhenius fit.

$\Delta \varepsilon(\alpha^*)$ are plotted against temperature in Figure 3.9, with $\Delta \varepsilon(\alpha)$ also shown for comparison purposes. $\Delta \varepsilon(\alpha^*)$ decrease significantly with increasing temperature, in keeping with that strong reduction in the number of hydrogen bonds with temperature. A qualitatively similar trend is observed for the infrared absorption associated with hydrogen bonding over the same temperature range, and in a previous DRS study of polybutadiene reversible networks [25]. The relaxation strengths of the $\alpha$ and $\alpha^*$
processes for SPS1H exhibit similar trends as a function of temperature, but the corresponding strengths are much smaller (the strengths of the $\alpha$ and $\alpha^*$ are about three and ten times smaller, respectively, than the comparable processes of SPS7H).

Figure 3.9. Temperature dependence of the dielectric relaxation strengths for the $\alpha$ and $\alpha^*$ processes of SPS7H (obtained from $\varepsilon''$ and $\varepsilon''_{SK}$ data, respectively).

3.4.4 Sub-$T_g$ Local $\beta$ Relaxation

PS does not exhibit a discernable dielectric $\beta$ process in the glassy state, due to the very small dipole moment associated with the pendant aromatic rings. However, SPS1H, SPS7H and SPS7CH$_3$ exhibit a well-defined, but weak process at $T < T_g$ (see
Figure 3.10). Considering the relative strengths of the processes for these three polymers, it is proposed that these β relaxations arise from the motion of the sulfonated phenyl groups in the glassy state. The possibility that this β relaxation is associated with water has been eliminated, because this process does not change in τ or Δε after SPS7H has been soaked in water (creating a specimen containing 2wt % of water). A relaxation associated with water is observed at very low frequency (below that of the β relaxation) at these temperatures.

![Dielectric loss spectra for SPS1H, SPS7H, and SPS7CH3 at 50 °C.](image)

**Figure 3.10.** Dielectric loss spectra for SPS1H, SPS7H, and SPS7CH3 at 50 °C.

As seen in Figure 3.11a, the β process exhibits the expected Arrhenius behavior, with the same activation energy (Eₐ ~ 65 kJ/mol) for SPS1H, SPS7H and SPS7CH₃. The relaxation strengths increase in the series SPS7H > SPS7CH₃ > SPS1H, in keeping with
sulfonation level and the increased dipole moment of the acid form. Relaxation strengths increase slightly with temperature due to greater dipole mobility at higher temperatures.

**Figure 3.11.** Temperature dependence of (a) the relaxation times and (b) the dielectric relaxation strengths for the β processes of SPS1H, SPS7H, and SPS7CH₃. The dotted line in (a) represents an Arrhenius fit.
3.5 Summary

The dynamics of model SPS copolymers, ionomer precursors, were investigated using dielectric relaxation spectroscopy, along with several complementary techniques. The glass transitions of the copolymers under investigation were found to increase slightly with sulfonation level due to increased steric hindrance resulting from the addition of sulfonate groups. FT-IR results confirmed the polymer chemistry and were also used to investigate the relative fraction of protonated and SO$_3^-$ species as a function of temperature. Results from DMA experiments indicated a slight shift of the mechanical $\alpha$ relaxation to higher temperatures and demonstrated that H-bonding leads to a significant increase in the temperature range of the rubbery plateau.

Four well-defined processes were observed in dielectric spectra of the acid forms of sulfonated PS. The fragility was found to be approximately constant for all sulfonation levels, attributed to the relatively high level of intermolecular cooperativity for PS. Two relaxations were observed at temperatures above the dielectric $\alpha$ process, and attributed to electrode polarization and a relaxation associated with H-bond association/disassociation. The relaxation strength of the $\alpha^*$ process decreased rapidly at temperatures above 160 $^\circ$C, in keeping with the reduction of H-bonding at higher temperatures, as demonstrated in FT-IR experiments. A local $\beta$ relaxation was observed in the dielectric spectra of the chemically modified PSs and assigned to the motion of the sulfonated phenyl groups.
3.6 References

5. Li, C.; Register, R.A.; Cooper, S.L. *Polymer* 1989, 30, 1227.


Chapter 4

Dynamics of Sulfonated Polystyrene Ionomers Using Broadband Dielectric Spectroscopy

In Chapter 3, the analysis of the dielectric relaxation behavior of the SPS copolymers in acid form have been reported. In this chapter the dynamics of the neutralized versions, SPS-Na, SPS-Cs and SPS-Zn having 7 mol % sulfonation, are demonstrated.

4.1 Glass Transition Behavior

A single glass transition (T_g) was observed for all SPS ionomers. A second higher temperature transition is not detected (however, see discussion of DMA results to follow). This is not surprising since similar behavior have been reported by many other groups [1-5]. The T_g of SPS7Na is higher than SPS1Na due to the higher degree of sulfonation (Table 4.1). T_g's of the SPS7-M ionomers are slightly higher than SPS7H resulting from physical crosslinking, and no effect of counterion type on T_g was observed at the same sulfonation level [1-5].
4.2 FTIR Study

Figure 4.1 displays FTIR spectra of SPS7H and the corresponding ionomers between 950 and 1300 cm$^{-1}$. The arrows denote the positions of the bands associated with sulfonated species in proximity to the cations. The band assignments are provided in Table 4.2 [6,7]. As seen in Figure 4.1, the doublet at ~1200 cm$^{-1}$ and the absorption at 1042 cm$^{-1}$ are attributed to the antisymmetric and symmetric stretching vibration of the S-O bond of the $-$SO$_3$M$^+$, respectively. The bands at 1128 and 1011 cm$^{-1}$ result from the in-plane skeletal vibration of benzene rings substituted by SO$_3$ and SO$_3$M, respectively [6,7]. The splitting of the antisymmetric stretching vibration is due to either cations polarizing the anion asymmetrically or cations located on a single oxygen atom (see Table 4.2) [6,7]. Furthermore, the FTIR spectra permit an estimate of the energy of ion pairs; the greater the strength of the electrostatic interaction of a given ion pair, the larger

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS7H</td>
<td>110</td>
</tr>
<tr>
<td>SPS1H</td>
<td>106</td>
</tr>
<tr>
<td>SPS1Na</td>
<td>106</td>
</tr>
<tr>
<td>SPS7Na</td>
<td>116</td>
</tr>
<tr>
<td>SPS7Cs</td>
<td>117</td>
</tr>
<tr>
<td>SPS7Zn</td>
<td>115</td>
</tr>
</tbody>
</table>
the splitting of antisymmetric stretching vibration [6,8]. The results show a small difference in splitting, which leads to estimates of the electrostatic interaction strength of the ion pairs in the series Zn$^{2+}$ > Na$^+$ > Cs$^+$ [6].

Figure 4.1. FTIR spectra of SPS7H, SPS7Na, SPS7Cs, and SPS7Zn.
Table 4.2. FTIR absorption peaks and assignments of SPS-M [6,7].

<table>
<thead>
<tr>
<th>Absorbance band</th>
<th>SPS1Na</th>
<th>SPS7Na</th>
<th>SPS7Cs</th>
<th>SPS7Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$M$^+$, sym</td>
<td>1040</td>
<td>1042</td>
<td>1033</td>
<td>1039</td>
</tr>
<tr>
<td>SO$_3$M$^+$, asym</td>
<td>1226</td>
<td>1225</td>
<td>1220</td>
<td>1221</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>1199</td>
<td>1199</td>
<td>1199</td>
<td>1193</td>
</tr>
<tr>
<td>SO$_3$M</td>
<td>1128</td>
<td>1128</td>
<td>1127</td>
<td>1128</td>
</tr>
</tbody>
</table>

4.3 DMA Measurements

Figure 4.2a and b display storage and loss moduli respectively as a function of temperature for the SPS ionomers, compared with to the behavior of SPS7H. Results from DMA are not compared directly to those from dielectric measurements since the DMA frequency window is relatively small (0.01-100 Hz), and temperature scans are typical and were employed here. DMA is used in the current work to assist in assigning DRS relaxation processes (see section 4.5).

All ionomers exhibit a rubbery plateau (Figure 4.2a) above the temperature of the $\alpha$ process, as expected for systems in which ionic clusters provide physical crosslinks. The plateau moduli of SPS7Na and SPS7Cs are higher than SPS7Zn, indicating that the distance between physical crosslinks increases for divalent cations [9] and the lower ionic
strength of Na\textsuperscript{+} and Cs\textsuperscript{+} [3]. The rubbery plateau of SPS7Zn is slightly longer than SPS7Na, and considerably longer than SPS7Cs [10]. This is consistent with the relative strengths of ion pairs in the ionic aggregates of Zn\textsuperscript{2+} > Na\textsuperscript{+} > Cs\textsuperscript{+} [3,10] and in keeping with the FTIR results discussed above. Loss modulus spectra (Figure 4.2b) clearly show two transitions for all SPS ionomers. In contrast, no transition at temperatures above the mechanical \(\alpha\) relaxation, associated with segmental motion, was observed for SPS7H [11]. The high temperature transitions have been proposed to arise from segmental motions under constraint from ionic aggregates, and have been referred to as \(\alpha_2\) relaxations [2,3,12]. The approximate magnitudes of the \(\alpha_2\) relaxations of SPS7Na and SPS7Cs are higher than that of SPS7Zn and it has been proposed that chain segments attached to ionic clusters in SPS7Na and SPS7Cs are less restricted than those in SPS7Zn [9]. According to thermogravimetric analysis (TGA) and FTIR experiments, all ionomers are thermally stable below 250 °C, with no weight loss up to 350 °C (TGA) and no significant changes in chemical structure over the temperature range 100 to 250 °C (FTIR).
Figure 4.2. (a) Storage and (b) loss moduli versus temperature for SPS7H, SPS1Na, SPS7Na, SPS7Cs and SPS7Zn at 1Hz. The error bars represent the 95% confidence interval for the data of all samples.
4.4 SAXS Measurements

It has been demonstrated in previous SAXS studies of ionomers that the resulting scattering (phase separated morphology) depends strongly on the method of sample preparation and thermal history [1,12,13-15]. An ‘ionomer scattering peak’ is observed for SPS7Zn at $q = 0.04 \ \AA^{-1}$ (Figure 4.3), which is attributed to the presence of ionic aggregates in the PS matrix [12,16]. The mean interdomain spacing for SPS7Zn prepared in this way is $\sim 15 \ \text{nm}$ [14]. However, no such scattering peak was observed for SPS7Cs, SPS7Na or SPS1Na, although the scattering at very small angles is much greater than that of neat PS (see the inset in Figure 4.3) [1,13-15,17]. Similar results have been reported, and it has been proposed that the small angle upturn is associated with long-range inhomogeneity of the metal ions [1,13-15,17]. Some earlier investigations of Cs and Na forms of SPS ionomers [12,18] reported SAXS ‘ionomer peaks’ at $q \sim 0.17 - 0.18 \ \AA^{-1}$ but due to the higher angular detector limit of our SAXS experiments, it is unable to interrogate the scattering above $0.15 \ \AA^{-1}$. In addition, only the amorphous halos were observed by WAXD for all samples and the angular range of the WAXD experiments did not overlap with that of SAXS.
Figure 4.3. SAXS profile of SPS7Zn measured at room temperature. Inset: SAXS profile for PS, SPS1Na, SPS7Na and SPS7Cs at room temperature.
4.5 DRS

4.5.1 Segmental $\alpha$ Process

The segmental relaxation times and dielectric relaxation strengths of PS, unneutralized SPS, and the SPS ionomers were obtained by fitting the isothermal dielectric loss $\varepsilon''(f)$ curves with the Havriliak-Negami (HN) function [19], together with a contribution to the loss from dc conductivity when appropriate. Figure 4.4 shows dielectric loss spectra of SPS7Zn, after subtraction of conduction losses, at several temperatures. The segmental relaxation times ($\tau_{\text{max}}$) of all samples follow a Vogel-Fulcher-Tammann (VFT) form, $\tau_{\text{max}} = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$ [20], as expected (see Figure 4.5).

Fitting the VFT expression to the data for the SPS ionomers (using a constant $\tau_0 = 10^{-14}$ s) yields values of $B$ between 0.19 – 0.29 eV and $T_0$ between 12 – 35 °C. Similar to earlier results on the influence of hydrogen bonding on the segmental dynamics of SPS7H, the intermolecular cooperativity of SPS ionomers is not significantly affected by the physical crosslinking imparted by the ion clusters [11].
Figure 4.4. Dielectric loss spectra of SPS7Zn, after subtraction of conduction losses, at selected temperatures.
A comparison of the dielectric $\alpha$ ($\alpha_1$) processes of the ionomers and unneutralized SPS at $T_g + 35$ °C is displayed in Figure 4.6. The slight broadening at low frequencies for SPS7Zn and SPS7Na is likely due to constraints associated with the ionic aggregates. The high frequency broadening of SPS7Cs, and particularly SPS7Na, arises from overlap with local processes. While the dielectric $\alpha$ relaxation strengths, $\Delta\varepsilon(\alpha)$, of SPS7H and the ionomers change insignificantly over the temperature range investigated, $\Delta\varepsilon(\alpha)$ at $T_g + 80$ °C varies significantly between materials: the strength of the $\alpha$ process for SPS7H (0.71) is significantly higher than that of SPS7Zn (0.49), SPS7Na (0.44) and SPS7Cs (0.33). $\Delta\varepsilon(\alpha)$[SPS7H] contains a contribution from the polar acid groups and, although there is a
small quantity of unneutralized acid remaining in the ionomers and likely some neutralized species remaining in the matrix phase, clustering occurs and inhibits movement of some segments in or near clusters. Such segments presumably relax at much higher temperatures, i.e., are associated with the mechanical $\alpha_2$ process. As noted below, $\alpha_2$ processes were only observed in DMA experiments, not dielectric. The $\alpha_2$ processes cannot be observed in dielectric spectra, even in the Kramers-Kronig transformed spectra discussed below, since they are overwhelmed by the contribution of electrode polarization to $\varepsilon''$ and $\varepsilon'$ at temperatures of 200 °C and above.

Figure 4.6. Normalized (by $\varepsilon''_{\text{max}}$ and $f_{\text{max}}$) dielectric $\alpha$ processes of SPS7H, SPS7Na, SPS7Cs and SPS7Zn at $T_g + 35$ °C.
The dielectric loss $\varepsilon''$ was also obtained by transforming the dielectric constant $\varepsilon'$ via a numerical version of the Kramers-Kronig (KK) transform, $\varepsilon''_{KK}$ (see chapter 2 Eq. 2.2). This is particularly helpful for identifying dipole relaxations in regions of dielectric loss spectra having high conduction losses. For example, $\varepsilon''$, $\varepsilon''_{KK}$ and $\varepsilon'$ spectra of SPS7Zn at $T_g + 80 \, ^\circ\text{C}$ are compared in Figure 4.7 (SPS7Cs, SPS7Na and SPS1Na are similar and not shown). Two additional relaxation processes are clearly observed at temperatures above the dielectric $\alpha$ relaxation for all ionomers, as demonstrated in Figure 4.8. Their proposed origin is discussed in the next sections.
Figure 4.7. Dielectric spectrum of SPS7Zn at $T_g + 80$ °C: (a) the dielectric loss $\varepsilon''$ (open symbols) compared with the calculated $\varepsilon''_{KK}$ (filled symbols) spectrum, and (b) the dielectric constant $\varepsilon'$ spectrum.
The high loss and dielectric constant associated with the highest temperature – low frequency process clearly identifies it as originating from electrode polarization (EP), which arises from the accumulation of mobile ions at electrode interfaces (see Figure 4.7, for SPS7Zn) [11,21]. Due to the relatively high T_g's of the SPS ionomers, α_{EP} was only observed in a temperature range from 190 to 220 °C.

**Figure 4.8.** The ε''_{KK} spectra vs frequency at T_g + 80 °C of SPS7H, SPS7Na, SPS7Cs and SPS7Zn, indicating the segmental (α), Maxwell-Wagner-Sillars (α_{MWS}), and electrode polarization (α_{EP}) processes.

### 4.5.2 Electrode Polarization: α_{EP} Process

The high loss and dielectric constant associated with the highest temperature – low frequency process clearly identifies it as originating from electrode polarization (EP), which arises from the accumulation of mobile ions at electrode interfaces (see Figure 4.7, for SPS7Zn) [11,21]. Due to the relatively high T_g's of the SPS ionomers, α_{EP} was only observed in a temperature range from 190 to 220 °C.
4.5.3 Maxwell-Wagner-Sillars (MWS) Interfacial Polarization: $\alpha_{\text{MWS}}$

The $\alpha_{\text{MWS}}$ process is located between the dielectric $\alpha$ and $\alpha_{\text{EP}}$ processes and it might at first seem reasonable to assign it to motions analogous to the DMA $\alpha_2$ relaxation. However the DMA $\alpha_2$ process is observed at a much higher temperature (50-70 °C higher) at the same frequency (see the isochronal plot in Figure 4.9 for example). As noted earlier, there is a very small amount (< 0.3 wt %) of residual water in the samples, presumably in ‘bound’ form, but there is no evidence in the literature for a relaxation for bound water in the frequency range of these measurements. Therefore, since many previous findings as well as those in the present paper support the two phase nature of SPS ionomers, it is proposed that this process is a manifestation of Maxwell-Wagner-Sillars (MWS) interfacial polarization, which arises in multiphase systems in which the phases have different dielectric constants and conductivities [22].
The dielectric relaxation strengths of the $\alpha$, $\alpha_{\text{MWS}}$ and $\alpha_{\text{EP}}$ processes and the activation energy of the segmental process at $T_g + 80 \, ^\circ\text{C}$ are provided in Table 4.3. From VFT equation, the apparent $\alpha$ activation energy is obtained as $E_{\text{app}}(T) = B/(1-T_o/T)^2$ [23]. $E_a$ for $\alpha_{\text{MWS}}$ (~100 kJ/mol) and $\alpha_{\text{EP}}$ are not included in Table 4.3 because they are not physically meaningful.

Figure 4.9. Cross plot of dynamic mechanical and dielectric loss $\varepsilon''_{\text{KK}}$ as a function of temperature for SPS7Na at 1 Hz.
The MWS relaxation times for SPS7Zn exhibit a non-Arrhenius temperature dependence, as shown in Figure 4.10, but the form of the temperature dependence for SPS7Na and SPS7Cs is uncertain due to the relative lack of data points. The $\alpha_{\text{MWS}}$ relaxation time for SPS1Na is not shown since the strength of the $\alpha_{\text{MWS}}$ process is quite small for this material (consistent with its assignment as an MWS process) and at some temperatures it overlaps with the segmental process. Finally, although in principle one can use the characteristics of the observed MWS processes to extract information about the nature of the phase separated clusters, the MWS models needed to do so have too many unknown parameters to make this a worthwhile exercise.

### Table 4.3. Dielectric relaxation strength of the $\alpha$, $\alpha_{\text{MWS}}$, $\alpha_{\text{EP}}$ processes, and the activation energy of the $\alpha$ process at $T_g + 80$ °C for SPS7M.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \varepsilon(\alpha)$</th>
<th>$\Delta \varepsilon(\alpha_{\text{MWS}})$</th>
<th>$\Delta \varepsilon(\alpha_{\text{EP}})$</th>
<th>$E_a(\alpha)$, [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS7Na</td>
<td>0.44</td>
<td>1.85</td>
<td>10.5</td>
<td>184</td>
</tr>
<tr>
<td>SPS7Cs</td>
<td>0.33</td>
<td>1.32</td>
<td>5.3</td>
<td>189</td>
</tr>
<tr>
<td>SPS7Zn</td>
<td>0.49</td>
<td>0.95</td>
<td>67</td>
<td>191</td>
</tr>
</tbody>
</table>
Unlike neat PS, SPS7H and its Na, Cs and Zn ionomers exhibit relatively weak β relaxations (Figure 4.11). This process is not associated with residual water as was pointed out in Chapter 3. Even when samples were soaked in water (reaching ~2% water content), the relaxation time and strength of the β process remained unchanged. A new relaxation did appear at lower frequencies in this temperature range, but disappeared upon heating above 120 °C.

**Figure 4.10.** Relaxation times of the α_{MWS} process as a function of temperature for SPS7Na, SPS7Cs, and SPS7Zn.

### 4.5.4 Local β Relaxations

Unlike neat PS, SPS7H and its Na, Cs and Zn ionomers exhibit relatively weak β relaxations (Figure 4.11). This process is not associated with residual water as was pointed out in Chapter 3. Even when samples were soaked in water (reaching ~2% water content), the relaxation time and strength of the β process remained unchanged. A new relaxation did appear at lower frequencies in this temperature range, but disappeared upon heating above 120 °C.
Therefore, the $\beta$ process was assigned to the motion of the sulfonated phenyl groups in the glassy state [11]. SPS1Na exhibits a very weak $\beta$ relaxation due to the small amount of sulfonation (1 mol %). The $\beta$ relaxation strengths $\Delta\varepsilon(\beta)$, the shape parameters, and the activation energies of SPS7Na, SPS7Cs, SPS7Zn, and SPS7H, are displayed in Table 4.4. $\Delta\varepsilon(\beta)$ decreases in the order SPS7H > SPS7Cs > SPS7Na > SPS7Zn, suggesting that this local motion is suppressed in the ionomers by interaction with the cations that create the physical crosslinks. Furthermore, the relaxation times of the $\beta$ process decrease as SPS7H > SPS7Cs > SPS7Na > SPS7Zn as seen in Figure 4.12. The sequence of decreasing relaxation strengths and times follows the increased electrostatic

**Figure 4.11.** Dielectric loss spectra for SPS7H, SPS1Na, SPS7Na, SPS7Cs and SPS7Zn at 60 °C.
interaction energy of the ion pairs. The activation energies shown in Table 4.4 do not follow a trend based on ionic strengths.

**Table 4.4.** Dielectric relaxation strength, relaxation shape parameters and activation energy of the \( \beta \) relaxations at 60 °C of SPS-H and SPS-M.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \Delta \varepsilon(\beta) )</th>
<th>( m \cdot n )</th>
<th>( E_a(\beta), [\text{kJ/mol}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPS7H</td>
<td>0.55</td>
<td>0.18</td>
<td>69</td>
</tr>
<tr>
<td>SPS7Na</td>
<td>0.34</td>
<td>0.55</td>
<td>76</td>
</tr>
<tr>
<td>SPS7Cs</td>
<td>0.41</td>
<td>0.23</td>
<td>35</td>
</tr>
<tr>
<td>SPS7Zn</td>
<td>0.26</td>
<td>0.82</td>
<td>34</td>
</tr>
</tbody>
</table>

**Figure 4.12.** Temperature dependence of the relaxation times for the \( \beta \) processes of SPS7H, SPS7Na, SPS7Cs and SPS7Zn. The dotted line represents an Arrhenius fit.
4.6 Summary

The single glass transitions of SPS ionomers were observed to increase slightly from that of unneutralized SPS due to physical crosslinks created by ionic aggregates. FTIR and DMA results demonstrated qualitatively similar trends with the strength of the electrostatic interaction of the ion pairs in ionomers. The ionomers also exhibited a rubbery plateau in DMA experiments and a second transition above the mechanical $\alpha$ relaxation for all SPS ionomers, attributed to segmental motion under relatively severe constraint from the physical crosslinks. The mean interdomain spacing for SPS7Zn observed from SAXS was $\sim 15$ nm. The large upturn in scattering intensity at small angles for the ionomers has been proposed previously to be associated with the long-range inhomogeneity of the metal ions.

The dielectric spectra of the SPS ionomers revealed four relaxation processes. Three of these are observed above the glass transition temperature and attributed to the segmental relaxation ($\alpha$), and processes arising from Maxwell-Wagner-Sillars interfacial polarization and electrode polarization. The relaxation strength of the segmental $\alpha$ process of the SPS ionomers was found to be significantly lower than SPS7H due to the reduction in polar acid species and constraints imparted by physical crosslinks.

A local dielectric $\beta$ process was observed for SPS and the ionomers and assigned to the motion of sulfonated phenyl groups. The reduction in relaxation strength and slowing down of the $\beta$ process demonstrated the effect of physical crosslinks on decreasing the mobility of the sulfonated phenyl groups.
4.7 References


15. Grady, B.P.; Matsuoka, H.; Nakatani, Y.; Cooper, S.L.; Ise, N.


5.1 Introduction

Mixtures of solid polymers with various salts have been of interest for many years as possible membranes for lithium ion batteries and in other electrochemical applications. A variety of polymer - salt solutions has been investigated [1-25], particularly polyethylene oxide (PEO) and polypropylene (PPO) with lithium perchlorate (LiClO$_4$) [1-9]. Single phase polymer - salt systems have been reported in a number of cases based on findings from differential scanning calorimetry (DSC) [3,4,6,15-17,19] and dynamic mechanical analysis (DMA) measurements [24-27]. In contrast, microphase separation has been inferred in some cases from the observation of two glass transitions: in PPO - LiClO$_4$ mixtures when the salt concentration exceeds 10 mol% [3,14], in PPO - LiBr, PPO - NaI and PPO - NaClO$_4$ [3,4,14]. Microphase separation into relatively ion-rich and ion-depleted domains has been proposed from the observation of fast and slow dielectric segmental relaxations in PPO - LiClO$_4$ complexes [7].

The interaction between dissociated salt anions and polyethers is expected to be considerably weaker than the corresponding interaction between cations ether oxygen atoms, but anion conductivity nevertheless also demonstrates strong correlation with polymer motion [11,25]. Using molecular dynamic simulations, Borodin and Smith observed three mechanisms of Li$^+$ and bis-trifluoromethane anion (TFSI$^-$) transports in
amorphous PEO [10]: subdiffusive Li$^+$ motion along PEO chains, Li$^+$ motion together with PEO segments, and Li$^+$ intersegmental hopping with the anion acting as an intermediate bridge. In addition, motion of both Li$^+$ and TFSI$^-$ was found to be coupled with the segmental dynamics of PEO [10].

In an extension of our earlier work on polyether-salt solutions using broadband dielectric spectroscopy [15], in this present study we investigate ion conduction and polymer dynamics of poly(2-vinylpyridine) [P2VPy] - LiClO$_4$ mixtures containing 0.1 to 10 mol% LiClO$_4$. In order to relate the structural properties of the mixtures to the dynamics, DSC, FTIR, WAXD, DMA and SAXS are employed in a complementary role.

### 5.2 Glass Transition Behavior

A single $T_g$ was observed for neat P2VPy and all P2VPy - LiClO$_4$ mixtures as displayed in Figure 5.1. $T_g$ increases with LiClO$_4$ content from 107 °C for neat P2VPy to 142 °C for P2VPy containing 10 mol% LiClO$_4$ (see the inset of Figure 5.1). These results are similar to the reported increase in $T_g$ of P4VPy-zinc acetate [19]. A similar $T_g$ enhancement has also been observed for poly(vinyl methylether)(PVME) - LiClO$_4$ [15] and for PPO - AgCF$_3$SO$_3$ complexes [18]. The increase in $T_g$ results from lower chain mobility of the host polymers, due in this case to the Li$^+$⋯N interactions, which can lead to transient physical crosslinks [9,16]. Possible coordination bonding between P2VPy and LiClO$_4$ is represented in Figure 5.2 [6,11,16,20]. The comparative interaction strength between Li$^+$⋯N and Li$^+$⋯O can be estimated by the relative increase in $T_g$ of the mixtures. Based on previous work on PVME - LiClO$_4$ complexes [15], the relative
interaction strength of Li$^+$···N and Li$^+$···O is judged to be very similar, as $T_g$ increases 37 °C for a 10/100 PVME - LiClO$_4$ and 35 °C for the comparable P2VPy - 10Li complex. The broadening of $T_g$ region ($\Delta T_g$), defined as the temperature interval from the onset to the end of the process, increases slightly: from 6 °C for neat P2VPy to 10 °C for P2VPy - 10Li. (inset in Figure 5.1). This broadening indicates that LiClO$_4$ is well solvated in P2VPy and the local environment is relatively homogeneous, as supported also by the WAXD, SAXS, and DMA results to follow (see section 5.4).

Figure 5.1. DSC thermograms of P2VPy - LiClO$_4$ mixtures. The inset displays the $T_g$ and the breadth of the $T_g$ region as a function of LiClO$_4$ concentration.
5.3 State of P2VPy - Li⁺ Coordination using FTIR

Spectral features related to polymer - LiClO₄ interactions have been evidenced by FTIR absorption bands at ~624 and ~636 cm⁻¹, related to the vibration modes of the free ClO₄⁻ ions and the ClO₄⁻ and Li⁺ contact pair, respectively [1,6,21]. Unfortunately P2VPy displays a pyridine ring stretching mode within this region, so the quantitative analysis of the LiClO₄ – P2VPy interaction using this approach is not possible. An FTIR study of the P2VPy - Zn(ClO₄)₂ and P4VPy - Zn(ClO₄)₂ systems [16] has shown that the
absorbance of ‘free’ and coordinated pyridine rings appear within the spectral regions from 980-1040 cm\(^{-1}\).

Free and coordinated pyridine ring stretching modes for P2VPy - LiClO\(_4\) were clearly observed at ~993 and 1009 cm\(^{-1}\) respectively, as seen in Figure 5.3.

The absorbance due to the coordinated pyridine rings is only observed clearly when the concentration of LiClO\(_4\) is \(\geq 5\) mol %. It is not observed at lower salt content, presumably as a consequence of low salt content. The peaks at 993 and 1009 cm\(^{-1}\) were fit using a linear baseline and adjustable-width Gaussian - Lorentzian bandshapes [28].
The area fraction of the coordinated pyridine rings is 29 % for P2VPy - 10Li, approximately three times that of P2VPy - 5Li, which is ~ 10 %.

5.4 Analysis of Possible Phase Separation

**WAXD.** Figure 5.4a displays the WAXD patterns of P2VPy - LiClO₄ mixtures compared to neat P2VPy. The diffraction patterns of the mixtures do not display any diffraction peaks from crystalline LiClO₄, but rather only exhibit two broad amorphous halos. Previous research [16,17,29,30] has assigned the lower angle halo as arising from the mean intermolecular distance between the chains, d<sub>poly</sub> and the second to either the mean inter-pendant or intra- pendant group distance, d<sub>pend</sub>. The peak intensity of the higher angle halo has been found to be more prominent compared to the lower angle halo for polymers containing phenyl pendant groups such as polystyrene and its derivative [31-33], as well as P2VPy and P4VPy [16,17,34]. This is due to the more ordered-glassy structures when the intra-phenyl interactions between intrachain and interchain phenyl groups are present. The mean values of d<sub>poly</sub> and the d<sub>pend</sub> calculated from the Bragg relationship [35], \( d = \frac{\lambda}{2\sin\theta} \) are shown in Figure 5.4b. For neat P2VPy, d<sub>poly</sub> ~0.79 nm and d<sub>pend</sub> is ~0.46 nm. Values of d<sub>pend</sub> decrease slightly with increasing LiClO₄ content, which likely results from Li⁺ coordination creating transient crosslinks between pyridine groups. A corresponding small decrease in d<sub>poly</sub> is also observed for mixtures containing up to 5 mol % LiClO₄. However, d<sub>poly</sub> increases significantly at 10 mol% LiClO₄ suggesting that ClO₄⁻ ions dominate the behavior: these anions are weakly solvated and distributed among the polymer chains [11,16]. Similar results have been observed for
P2VPy - ZnClO$_4$, P4VPy - ZnClO$_4$ and poly(vinylpyrrolidone) (PVP) - AgClO$_4$ solutions [16,17]. Moreover at relatively high salt concentration, the appearance in peak broaden and lower intensity of the lower angle halo are observed, resulting from the variance of the free volume distribution and the reduction of the locally oriented amorphous chain segment, respectively [33].
Figure 5.4. (a) WAXD patterns and (b) interchain and pendant group distances of P2VPy - LiClO$_4$ as a function of LiClO$_4$ concentration.
DMA. Figure 5.5 presents the storage and loss moduli as a function of temperature for neat P2VPy and the P2VPy - LiClO₄. All materials exhibit a single mechanical loss peak corresponding to segmental motion (the α process), i.e., the dynamic Tᵢ [24-27]. The α relaxation shifts to higher temperatures with increasing LiClO₄ concentration, in accord with the behavior observed in DSC experiments. The observation of a single α process indicates a relatively homogeneous environment for the P2VPy - LiClO₄ mixtures at the segmental length scale (ca. 2-10 nm). Similar findings have been reported for PEO-Fe(SCN)₃, PEO - Ba(SCN)₂ [24,25], polyurethane - LiClO₄ [26], and ethylene oxide/ethyl glycidyl ether copolymer - LiPPI [27]. The magnitudes of the rubbery plateau modulus do not change significantly with LiClO₄ content, but the plateau increases somewhat in extent at the highest LiClO₄ concentrations, in line with some intermolecular bridging resulting from P2VPy - Li⁺ coordination.
Figure 5.5. (a) Mechanical storage $E'$ and (b) loss modulus $E''$ vs temperature for P2VPy and P2VPy - LiClO$_4$ mixtures at 1 Hz.
**SAXS.** The small-angle X-ray scattering curves (Figure 5.6) for the P2VPy-LiClO₄ solutions show no indication of microphase separation (i.e., no a scattering peak) for length scales ranging from 5-40 nm.

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![SAXS profiles of P2VPy - LiClO₄ mixtures measured at room temperature.](image)

**Figure 5.6.** SAXS profiles of P2VPy - LiClO₄ mixtures measured at room temperature.

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5.5 Dielectric Relaxation

5.5.1 Dielectric Relaxation of Sub-$T_g$ $\beta$ Process

P2VPy exhibits a strong and broad local relaxation in the glassy state due to the rotation of pyridine side-groups [34]. Figure 5.7 shows $\varepsilon''$, normalized by the concentration of P2VPy, all materials at 50 °C. Figure 5.8a and b display the $\tau_{\text{max}}$ and the
normalized dielectric strength (Δε) of the β process as a function of temperature, respectively. Δε(β) is suppressed with increasing Li⁺ content, precipitously so for LiClO₄ contents > 0.5 mol %. To the author’s knowledge, this is the first observation of β suppression (i.e., suppression of sub-nm scale motion) in polymer - salt mixtures, and such behavior has potential consequences for material mechanical behavior and mobility of small molecules in the glassy state. At least for higher LiClO₄ content mixtures, this finding is consistent with coordination of pyridine rings observed in FTIR spectra. There are two possible mechanisms for suppression of the β process: the formation of transient crosslinks, which effectively freeze the rotation of pyridine groups and leads to a corresponding decrease in the remaining ‘free’ pyridine side groups; and a reduction in the local free volume, which restricts pyridine group rotation.

The ‘residual’ β relaxations of the mixtures are somewhat slower than that of neat P2VPy, particularly for P2VPy - 5Li and P2VPy - 10Li. All β process exhibits Arrhenius behavior as expected, with approximately the same activation energy (Eₐ ~ 57 kJ/mol) for all mixtures, higher that that neat P2VPy (Eₐ ~ 41 kJ/mol). Therefore, even the motion of ‘free’ pyridine rings is influenced by the presence of Li⁺.
Figure 5.7. Dielectric loss spectra, normalized by the concentration of P2VPy, for P2VPy and P2VPy - LiClO$_4$ at 50 °C.
Figure 5.8. (a) Relaxation times (b) relaxation strengths normalized by P2VPy concentration, for the $\beta$ processes and of P2VPy and P2VPy - LiClO$_4$ as a function of temperature. The dashed lines indicate Arrhenius fits.
5.5.2 Relaxations above $T_g$

As an example of the dielectric relaxation behavior of the polymer – salt mixtures, Figure 5.9 displays $\varepsilon''$, $\varepsilon'$ and $\varepsilon''_{KK}$ of P2VPy - 0.5Li at 140 °C as a function of frequency. Three relaxations are observed, denoted as $\alpha_1$, $\alpha_2$ and $\alpha_3$ with increasing temperature. To clarify the processes above the $\alpha_1$ segmental process, $\tan \delta$ ($\tan \delta = \varepsilon''/\varepsilon'$) is plotted as a function of frequency in Figure 5.10a for P2VPy – LiClO$_4$ mixtures at $T_g + 35$ °C. Relative to $\varepsilon''$, the peak maxima in $\tan \delta$ are shifted to higher frequencies and the conductivity is suppressed [36], facilitating the observation of an additional process at low frequencies ($\alpha_4$). Four processes can be seen in Figure 5.10a, and these coincide with relaxations observed in $\varepsilon''_{KK}$. The $\alpha_4$ relaxation is observed for all P2VPy - LiClO$_4$ systems and shifts to higher frequency with increasing temperature (demonstrated in Figure 5.10b for P2VPy - 5Li).
Figure 5.9. Dielectric constant $\varepsilon'$, dielectric loss $\varepsilon''$ and $\varepsilon''_{KK}$ spectra of P2VPy - 0.5Li at 140 °C.
Figure 5.10. Tan δ as a function of frequency at (a) $T_g + 35\,^\circ C$ for P2VPy - LiClO$_4$ and (b) at selected temperatures above $160\,^\circ C$ for P2VPy - 5Li.
Figure 5.11 displays the relaxation map for the $\alpha_1$, $\alpha_2$ and $\alpha_3$ processes. At low ion concentrations, $\alpha_1$ displays similar relaxation times to that of the segmental motion in neat P2VPy. The relaxation shifts to longer times with increasing LiClO$_4$ content, in keeping with observations from DSC experiments.
Figure 5.11. Relaxation times of (a) the $\alpha_2$, and $\alpha_3$ process, and (b) the $\alpha_1$ process as a function of temperature. Dash lines indicate VFT fits to the data.
Based on the evidence presented earlier in this chapter, there is no phase separation in these mixtures. P2VPy strongly solvates LiClO₄, facilitated by interaction between pyridine groups and Li⁺ and generates homogeneous systems. Therefore, the possibility to Maxwell-Wagner-Sillars (MWS) interfacial polarization, arising in multiphase systems in which the phases have different dielectric constants and conductivities [37], is not the origin of any of the observed relaxations here. Furthermore, FTIR results do not display any reduction of the coordinated pyridine ring mode over the temperature range 100 to 250 °C, suggesting that Li⁺⋯N bond association and dissociation does not facilitate any relaxation above the α relaxation [38]. As demonstrated in Figure 5.10a, the relaxation strength of α₃ increases with salt concentration [2]. Similar relaxations have been observed for PPO – LiClO₄ mixtures and were assigned to an “ion-mode relaxation” [2,7,39,40] that was proposed to arise from the fluctuation of ions in the temporary confinements created by structural inhomogeneity [7,39,40]. The ions fluctuate inside the domain for a certain period and behave a Debye–type dielectric relaxation in the frequency domain [39,40]. The weak α₂ process is only observed in the spectra at a few temperatures for P2VPy - 0.1Li and P2VPy - 0.5Li, as it is obscured by the stronger α₃ process in all other situations. It is proposed that this process is associated with slow, hindered segmental motion [41]. The highest temperature process α₄ is clearly due to electrode polarization, as indicated by the high values of ε˝ and strong concurrent increases in ε’ (Figure 5.12) [36,38].
The relaxation times of the $\alpha_1$ processes follow the Vogel-Fulcher-Tammann (VFT) relation (Eq. 3.1), as shown by fits in Figure 5.12, and fitting parameters are provided in Table 5.1.

**Figure 5.12.** The dielectric constant as a function of frequency at selected temperatures of the P2VPy - 0.5Li mixture. The higher-frequency step represents $\alpha_3$ and the lower-frequency step represents $\alpha_4$. 
5.5.3 Conductivity

The complex permittivity can be converted to the complex conductivity \( \sigma^* = \sigma' + i\sigma'' \) via \( \sigma' = \omega \varepsilon'' \) and \( \sigma'' = \omega \varepsilon' \) [7]. Here, the conductivity \( \sigma_0 \) is determined from the low frequency plateau of the real part of conductivity. Figure 5.13 displays the conductivities as a function of temperature. At any particular temperature, values of \( \sigma_0 \) for all P2VPy - LiClO\(_4\) mixtures are rather similar. Conductivities as a function of T - T\(_g\) are displayed in Figure 5.14a. Conductivities are similar for P2VPy (the conductivity of neat P2VPy arising from ionic impurities) and the lower salt content mixtures, but increase at higher salt concentrations. Figure 5.14b shows that at temperatures above T\(_g\), conductivity increases strongly with salt concentration. These results are in accord with a
previous study of ion conduction in PPO mixed with relatively low LiClO₄ concentrations (< 10 mol %) [9].

**Figure 5.13.** Ionic conduction as a function of temperature for P2VPy - LiClO₄.
Figure 5.14. Ionic conduction (a) as a function of T -$T_g$ and (b) as a function of LiClO$_4$ concentration at $T_g + 40$ °C, $T_g + 60$ °C and $T_g + 80$ °C in P2VPy - LiClO$_4$ mixtures.
Correlation between ion conduction and polymer dynamics can be obtained through cross-plots of $\sigma_0$ and polymer relaxation times. The Debye-Stokes equation predicts, for ideal conduction of a sphere, through a viscous medium relaxing with characteristic time $\tau$, that $\sigma\tau \cong \text{const}$ [42]. In this ideal limit, therefore, strong coupling between polymer segmental motion and conduction should yield a log-log plot with a slope of $-1$. Experimental plots typically yield lines with constant slope for systems above $T_g$, although the exponent may deviate from $-1$ [42,43]. Figure 5.15 displays a double log plot of $\sigma_0$ and $\tau_{\text{max}}$ for the principle $\alpha_1$ segmental process.
The $\alpha_1$ process is closely coupled to ion motion in nearly all cases, as demonstrated by the observed slopes of $\sim -1$ for P2VPy mixed with 0.1, 0.5, 1, and 5 % LiClO$_4$: that is, at these concentrations, ions are predominantly transported by coupling with the $\alpha_1$ process. Only the highest salt concentration, P2VPy - 10LiClO$_4$, do the data deviates from this correlation (~0.6). This indicates the partial decoupling of the segmental and ion motions, in keeping with the large increase in conductivity at $T-T_g$ and in the mean interdistance between polymer chains observed from WAXD.

Figure 5.15. Correlation between conductivity and relaxation times of the segmental $\alpha_1$ relaxation. The solid line indicates a slope of $-1$. 
decoupling of polymer and ion motions have been previously observed when the concentration of salts is relatively high, which is due to an increase in the number of dissociated ions, and hence enhances the ion self-diffusion coefficient, somehow greater than of the polymer [9,11].

A number of previous experimental and simulation investigations have concluded that the measured conductivities for polymer-salt mixtures are dominated by anions [10,27,42-49]. Following from these studies, the conductivity of the P2VPy mixtures under investigation here undoubtedly are dominated by anion motion as well. In addition, some authors conclude that substantial coupling exists between anion diffusion and segmental polymer motion [10,44,45,49], whereas others find a degree of decoupling [5,27,50]. Here, it is concluded that anions diffuse through the matrix assisted by the segmental motion at LiClO₄ concentration ≤ 5 mol %, based on the strong correlation between \( \sigma_0 \) and \( \tau_1 \) in Figure 5.15. P2VPy-10Li displays the weak correlation between the anions and the polymer segmental motion and hence leads to increased conductivity.

5.6 Summary

P2VPy - LiClO₄ mixtures with LiClO₄ contents from 0.1 to 10 mol % are demonstrated to be relatively homogeneous, single phase systems from DSC, WAXD, DMA and SAXS results. An increase in \( T_g \) with salt content indicates reduced chain mobility of the host polymers. Results from FTIR spectroscopy demonstrate the coordination between LiClO₄ and P2VPy at relatively high LiClO₄ content. WAXD results indicate excellent dispersion of LiClO₄ in the polymer matrix for P2VPy mixtures.
P2VPy mixed with 10 mol % LiClO$_4$ demonstrate a significant increase in the mean intermolecular distance between polymer chains, induced by the distribution of ClO$_4^-$ ions among the polymer chains. The mean packing distance between pyridine pendant groups decreases with increasing LiClO$_4$ content, suggesting the formation of transient crosslinks via Li$^+$ coordination.

Five processes are observed in DRS spectra. Four are observed above the glass transition and attributed to the predominant segmental relaxation ($\alpha_1$), an ion-mode relaxation ($\alpha_3$), and electrode polarization ($\alpha_4$). By analogy with observations on other polymer – salt solutions, it is proposed that the weak $\alpha_2$ process arises from segments with relatively hindered motion. A local $\beta$ relaxation in glassy state is observed, arising from the motion of the pyridine pendant groups. The suppression of the $\beta$ relaxation with increasing Li$^+$ content is caused by either the formation of transient crosslinks leading to a subsequent decrease in the number of free pyridine groups, or the reduction in the local free volume in the presence of LiClO$_4$.

Again, by analogy with the findings from a number of other studies, of P2VPy - LiClO$_4$ ionic conductivity at LiClO$_4$ concentrations less than 10 mol % is likely dominated by the diffusion of anions through the matrix, and this motion is strongly correlated with the principle segmental motion. At 10 mol % LiClO$_4$, the partial decoupling of the segmental and anion motions plays an important role and leads to increased conductivity.
5.7 References


Chapter 6

Effect of Intermolecular Hydrogen Bonding on the Dynamics of Poly (2-vinylpyridine) Mixtures with Low Molecular Weight Phenolic Molecules

6.1 Introduction

The associative interactions of the hydrogen bond have been of key interest for many years and have been widely studied. Intermolecular hydrogen bonding has an important effect on the miscibility of the polymer blends and polymer-small-molecule mixtures [1-17]. In addition supramolecular assemblies [18-20] and polymer blend complexes [21-24] can be created through strong intermolecular hydrogen bonds.

Investigations of intermolecular coupling in polymers have frequently used dielectric spectroscopy. A dielectric relaxation associated with transient hydrogen bonds in polyisobutylene modified with urazoylbenzoic acid groups [25,26], in supramolecular assemblies composed of small molecules linked with hydrogen bonds [19], and in sulfonic acid polystyrene ([27], Chapter 3) has been observed at temperatures above the segmental $\alpha$ process. In addition, it has been found that the local dielectric $\beta$ process is suppressed in blends where strong intermolecular hydrogen bonding is present [13,15,16]. Furthermore, hydrogen bonds have been observed to slow down relaxation times and increase fragility of the segmental $\alpha$ process in polymer blends [15-17].

This present study explores the effects of the addition of small molecules capable of intermolecular hydrogen bonding on the dynamics of a host polymer. Dielectric relaxation spectroscopy is used to study mixtures of a series of low molecular weight
phenolic molecules containing one to six hydroxyl groups with poly(2-vinyl pyridine) (P2VPy). P2VPy was chosen for this study because of the proton acceptor ability of the pyridine pendant group, facilitating the formation of hydrogen bonds with proton donor molecules [18,24,28-31].

### 6.2 Glass Transition Behavior

A single $T_g$ was observed for all concentrations of P2VPy/EPh, P2VPy/BPM, P2VPy/DHN, P2VPy/MHM and P2VPy/HDP mixtures signifying relatively homogeneous mixing (acronyms and chemical structures of the low small molecule phenols are described in Chapter 2 but for reference they are redisplayed in Figure 6.1). Very similar $T_g$s are determined from DRS and DSC. $T_g$s from DRS are determined using VFT parameters ($T_g^{\text{DRS}} = T_{\text{ref}}$) (Eq 3.2 in Chapter 3). $T_g$ values obtained from DSC and DRS along with predictions of the Fox equation [32] are shown in Figure 6.2. The $T_g$ of P2VPy is 107 °C and $T_g$s of the small molecules, estimated from $T_m/1.3$ [13], are provided in Chapter 2. The classic but simple Fox equation predicts $T_g$ behavior of mixtures based on the weight fractions $w_1$ and $w_2$ and $T_g$s of the neat components

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

(6.1)

Experimental $T_g$s follow the prediction of Eq. 6.1 surprisingly well, particularly considering the approximate values of the small molecule $T_g$s.
Figure 6.1. Chemical structures of P2VPy, EPh, BPM, DHN, MHM and HDP.
The only exception to the correspondence with the Fox eqn is P2VPy mixed with 10 mol % HDP: this composition displays a $T_g$ much higher (129 °C) than that of neat P2VPy (107 °C) and neat HDP (28 °C). The extremely high $T_g$ of P2VPy/10HDP is likely due to complex formation as proposed previously for poly(4-vinylphenol) and P2VPy [16]. But why P2VPy/10HDP behaves differently than other P2VPy/HDP mixtures, and all other mixtures under investigation here is unclear at the present time. The P2VPy/HDP mixtures are generally discussed separately later in this chapter.

Figure 6.2. Glass transitions for P2VPy mixtures. Solid and unfilled symbols are $T_g$s of the mixtures obtained from DSC and DRS respectively. Solid lines indicate the $T_g$s calculated from the Fox equation.
6.3 Hydrogen Bonding

**FTIR.** FTIR spectroscopy was used to qualitatively characterize the type and strength of the hydrogen bond in these mixtures. Figure 6.3 displays spectra from 2400 - 3700 cm\(^{-1}\) for selected P2VPy/EPh, P2VPy/BPM, P2VPy/DHN and P2VPy/MHM mixtures, the absorbance at ~3000 cm\(^{-1}\) corresponds to intermolecular –OH∙∙∙N bonding [34]. Unfortunately in the present cases, this peak overlaps with the CH stretching vibrations of P2VPy, inhibiting quantification [34]. The broad bands in the region from 3300 to 3400 cm\(^{-1}\) represent the intermolecular –OH∙∙∙O bonding present in the neat EPh, BPM, DHN and MHM.

Two trends are observed depending on the number of hydroxyl groups per small molecule. P2VPy/EPh does not exhibit a strong –OH∙∙∙O absorption with increasing EPh concentration, but the –OH∙∙∙N band increases slightly (Figure 6.3a) [9]. Both the –OH∙∙∙O and –OH∙∙∙N bands increase noticeably in P2VPy/BPM, P2VPy/DHN and P2VPy/MHM (Figure 6.3b-d).
Figure 6.3. FTIR spectra of P2VPy mixed with (a) EPh (b) BPM (c) DHN (d) MHM and (e) HDP at 10, 30 and 50 mol %. 
**WAXD.** Figure 6.4 presents the WAXD patterns of P2VPy mixed with 10 and 50 mol % small molecules. The lack of crystalline peaks indicates that the small molecules are well-dispersed in the host polymer. Two amorphous halos were observed for neat P2VPy and the mixtures, which the lower and higher angle halos corresponding to the mean packing distance between polymer chains and pyridine pendant groups, respectively (Chapter 5) [35-38]. The peak intensity of the higher angle halo has been found to be more prominent compared to the lower angle halo for polymers containing phenyl pendant groups such as polystyrene and its derivative [29,30,33], as well as P2VPy and P4VPy [35,36,40]. This is due to the more ordered-glassy structures when the intra-phenyl interactions between intrachain and interchain phenyl groups are present. The location of the two amorphous halos remains approximately the same for all mixtures except those with EPh. The shift of the amorphous halos to higher angle for P2VPy/EPh mixtures indicates that EPh assists the packing of polymer chains (over the length scale ranging from 0.5-0.7 nm) and hence reduce free volume [33]. In addition, the broader peaks observed, particularly the lower angle halo, have been proposed to reflect the variance of the free volume distribution [33].
SAXS. No scattering peak was observed for any of the P2VPy/EPh, P2VPy/BPM, P2VPy/DHN and P2VPy/MHM mixtures (Figure 6.5), indicating no discernable microphase separation at the length scales probed in these experiments.
Figure 6.5. SAXS profiles of (a) P2VPy/HDP at 10, 30 and 50 mol % of HDP and (b) P2VPy mixed with 10 mol% of EPh, DHN, MHM and HDP.

6.4 Dielectric Relaxation of Mixtures

6.4.1 Segmental Relaxations

Figure 6.6 presents the relaxation time $\tau_{\text{max}}$ of the segmental $\alpha$ process as a function of temperature for the five mixtures under consideration. The relaxation times of all samples are well fit by the Vogel-Fulcher-Tammann (VFT) relation (Eq 3.1). The fitting parameters $B$ and $T_0$ are provided in Table 6.1.
Figure 6.6. Relaxation times of the $\alpha$ process as a function of temperature for P2VPy and all mixtures. Dashed lines indicate VFT fits.
The segmental relaxation times of all three concentrations of P2VPy/EPh are faster than that of neat P2VPy and increase with increasing EPh concentration. The breadth of the segmental relaxation time distribution of P2VPy/EPh remains the same as of neat P2VPy (Figure 6.7a). The slight broadening at high frequencies is due to the low-frequency tail of the local $\beta$ relaxation process. The same behavior has been observed for mixtures of PVME with EPh [13], and was attributed to the absence of interchain cooperativity in the small molecule portion of the mixture and the promotion of a homogeneous environment encouraged by intermolecular hydrogen bonding.

### Table 6.1. VFT fit parameters for P2VPy and all mixtures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VFT parameters</th>
<th>T$_0$(°C)</th>
<th>B(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2VPy</td>
<td></td>
<td>22</td>
<td>0.22</td>
</tr>
<tr>
<td>10 EPh</td>
<td></td>
<td>-39</td>
<td>0.28</td>
</tr>
<tr>
<td>30 EPh</td>
<td></td>
<td>-47</td>
<td>0.24</td>
</tr>
<tr>
<td>50 EPh</td>
<td></td>
<td>-47</td>
<td>0.22</td>
</tr>
<tr>
<td>10 BPM</td>
<td></td>
<td>27</td>
<td>0.15</td>
</tr>
<tr>
<td>30 BPM</td>
<td></td>
<td>19</td>
<td>0.18</td>
</tr>
<tr>
<td>50 BPM</td>
<td></td>
<td>14</td>
<td>0.17</td>
</tr>
<tr>
<td>10 DHN</td>
<td></td>
<td>5</td>
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</tr>
<tr>
<td>30 DHN</td>
<td></td>
<td>27</td>
<td>0.20</td>
</tr>
<tr>
<td>50 DHN</td>
<td></td>
<td>36</td>
<td>0.19</td>
</tr>
<tr>
<td>10 MHM</td>
<td></td>
<td>31</td>
<td>0.22</td>
</tr>
<tr>
<td>30 MHM</td>
<td></td>
<td>47</td>
<td>0.18</td>
</tr>
<tr>
<td>50 MHM</td>
<td></td>
<td>51</td>
<td>0.16</td>
</tr>
<tr>
<td>10 HDP</td>
<td></td>
<td>71</td>
<td>0.19</td>
</tr>
<tr>
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</tr>
<tr>
<td>50 HDP</td>
<td></td>
<td>-30</td>
<td>0.30</td>
</tr>
</tbody>
</table>
bonding between P2VPy and EPh [13]. Figure 6.8a displays the dielectric relaxation strength ($\Delta \varepsilon$) of P2VPy/EPh mixtures compared to neat P2VPy at T-$T_g$. $\Delta \varepsilon$ increases with EPh concentration. Increase in $\Delta \varepsilon$ with increasing concentration also has been observed previously for poly(vinyl methyl ether) (PVME) and EPh mixtures [13]. This indicates that the rotational reorientation of EPh molecules is coordinated with the segmental relaxation and hence increases the average dipole moment of the host polymers.
Figure 6.7. Normalized segmental $\alpha$ processes of the mixtures (a) P2VPy/EPh, (b) P2VPy/BPM, (c) P2VPy/DHN, (d) P2VPy/MHM and (e) P2VPy/HDP at $T_g + 40^\circ$C.
Figure 6.8. Dielectric strengths for the $\alpha$ processes of (a) P2VPy/EPh, (b) P2VPy/BPM (c) P2VPy/DHN (d) P2VPy/MHM and (e) P2VPy/HDP mixtures.
**P2VPy/BPM, P2VPy/DHN and P2VPy/MHM mixtures.** Relaxation times of P2VPy/BPM are faster than that of neat P2VPy. Those of P2VPy/DHN are almost the same as that of neat P2VPy for 10 and 30 mol %, and become slightly faster at 50 mol %. P2VPy/MHM at 10 mol % is slightly slower than neat P2VPy, almost the same at 30 mol % and become slightly faster at 50 mol % (Figure 6.6). These behaviors are consistent with results from DSC experimental discussed earlier: $T_g$s of P2VPy/BPM mixtures decreases with increasing BPM concentration, remain unchanged for P2VPy/DHN and decreases slightly for P2VPy/MHM mixtures. Moreover, the breadths of the $\alpha$ relaxations of P2VPy/BPM, P2VPy/DHN and P2VPy/MHM mixtures increase with concentration of phenolic molecules and are broader than for neat P2VPy, particularly at 30 and 50 mol %, as seen in Figure 6.7. No significant changes in the breadths of the $\alpha$ relaxations with the number of hydroxyl groups of these mixtures, having 2 and 4 hydroxyl groups at any compositions (Figure 6.9). Therefore in contrast with P2VPy/EPh, this suggests that P2VPy mixed BPM, DHN and MHM at concentrations above 10 mol % exhibit some degree of dynamic heterogeneity [11,12]. Similar to P2VPy/EPh, $\Delta\varepsilon$ of P2VPy/BPM and P2VPy/DHN also increase with BPM and DHN concentration (Figure 6.8b and 6.8c). $\Delta\varepsilon$ of P2VPy/MHM at 30 and 50 mol % increases with increasing temperatures, in general, indicating that segmental cooperativity is enhanced by thermal energy.
**Figure 6.9.** Normalized segmental $\alpha$ processes of the mixtures of (a) 10 mol %, (b) 30 mol % and (c) 50 mol% of EPh, BPM, DHN, MHM and HDP at $T_g + 40^\circ C$. 
6.4.2 Relaxation above the Segmental Process

As described in Chapters 3, 4, and 5, relaxations above the segmental relaxation can be explored by calculating the conduction-free dielectric loss $\varepsilon''_{kk}$ from $\varepsilon'$, using a numerical version of the Kramers-Kronig (KK) transform (Eq 2.2). The segmental $\alpha$ relaxation and what is subsequently referred to as the $\alpha'$ relaxation are observed in all mixtures: Figure 6.10a shows P2VPy/EPh as a characteristic example. Very large values of dielectric constant (Figure 6.10b) and loss indicate that the $\alpha'$ process is associated with electrode polarization (see Chapter 3 for more details).
Figure 6.10. (a) The $\varepsilon''_{KK}$ spectra and (b) the dielectric constant $\varepsilon'$ as a function of frequency for P2VPy, P2VPy/10EPh, P2VPy/30EPh and P2VPy/50EPh at $T_g + 40$ °C.
6.4.3 Local β Relaxations

P2VPy exhibits a strong and broad local relaxation due to the rotation of pyridine side-groups [40]. Figure 6.11 presents the dielectric loss spectra, normalized by the concentration of P2VPy at -20 °C, of neat P2VPy, P2VPy/EPh, P2VPy/DHN, P2VPy/BPM, P2VPy/MHM and P2VPy/HDP mixtures as representative examples. The strength of the β process decreases significantly from neat P2VPy with increasing small-molecule concentration, observed, except P2VPy mixed with 30 and 50 mol % EPh.
Figure 6.11. Dielectric loss spectra normalized by P2VPy concentration at -20 °C for (a) P2VPy/EPh (b) P2VPy/DHN (c) P2VPy/BPM (d) P2VPy/MHM and (e) P2VPy/HDP at 10, 30 and 50 mol %.
The dielectric strength $\Delta \varepsilon(\beta)$ provides a measure of the degree of suppression of the $\beta$ process. Figure 6.12 shows that the $\beta$ process is suppressed with the addition of all concentrations of DHN, BPM, MHM, HDP as well as 10 mol% EPh, but not with the addition of 30 and 50 mol% EPh. Values of $\Delta \varepsilon(\beta)$ for P2VPy mixed with 50 mol% of BPM and DHN, 30 and 50 mol% of MHM and HDP are not shown since they are completely suppressed.

EPh contains one hydroxyl group, and interacts with pyridine groups without bridging pyridine rings. Therefore, the pyridine groups are relatively free to rotate. An increase in dipole moment of a pyridine ring bonding with a phenol group has been previously determined by means of measuring the total polarization of sample in the gas phase [41]. Instead of increasing $\Delta \varepsilon(\beta)$ of P2VPy/10EPh due to increasing a dipole moment, a decrease in $\Delta \varepsilon(\beta)$ is observed. This suggests that the suppression of $\beta$ process is more likely effected by a reduction in the local free volume, keeping with WAXD results, and hence the rotation of pyridine groups is restricted. At first it might seem the apparent increase in $\Delta \varepsilon(\beta)$ for P2VPy mixed EPh at 30 and 50 mol% arises from an increase in a dipole moment of pyridine bonded with EPh. However the values of $\Delta \varepsilon(\beta)$ increase significantly with temperatures. To develop a better understanding of the apparent increase in $\Delta \varepsilon(\beta)$ for P2VPy/30EPh and P2VPy/50EPh, the relaxation of neat EPh was experimentally studied, for the first time to the authors knowledge. At temperatures below $T_g$ of EPh, neat EPh exhibits a very strong local relaxation (Figure 6.13a), which can be compared with previously results on isoeugenol (structure similar to EPh) in which a similar transition was assigned to a Johari-Goldstein (JG) $\beta$
relaxation [42]. The JG relaxation involves the entire molecule and behaves similarly to the $\alpha$ relaxation. A comparison of neat P2VPy, neat EPh, with P2VPy with 30 and 50 mol % EPh is shown in Figure 6.13b and clearly demonstrates the overlap of the P2VPy local motion with the JG relaxation of neat EPh, consistent with the increase in strength with EPh concentration in the 30 and 50 mol% mixtures. Therefore the increase in $\Delta\varepsilon(\beta)$ with either temperature or EPh concentration of P2VPy/30EPh and P2VPy/50EPh mixtures is associated with the $\beta$ process of neat EPh.
Figure 6.12. Dielectric strengths for the $\beta$ processes of (a) P2VPy/EPh at 10, 30 and 50 mol% EPh, (b) P2VPy/BPM at 10, 30 mol% BPM, (c) P2VPy/DHN at 10, 30 mol% DHN and (d) P2VPy with 10 mol % EPh, BPM, DHN, MHM and HDP.
The presence of two or more hydroxyl groups per molecule leads to the possibility of formation of transient hydrogen bonding between polymer chains and these are likely the origin of the suppression of the $\beta$ process in these mixtures. This is similar to the observed suppression of the $\beta$ relaxation for the polymer - salt mixtures discussed.

Figure 6.13. Dielectric loss spectra for (a) neat EPh at selected temperature below -30 °C and (b) neat P2VPy compared to neat EPh, P2VPy mixed with 30 and 50 mol % EPh at -20 °C.
in Chapter 5. It was also proposed that this involved the formation of transient crosslinks, which restricts the rotation of pyridine groups and leads to a decrease in the remaining free pyridine groups [43]; and a reduction in the local free volume, which restricts the rotation of pyridine groups.

\( \beta \) relaxation times follows an Arrhenius temperature dependence, as shown in Figure 6.14. The \( \beta \) processes for P2VPy mixed with 50 mol % of BPM and DHN, 30 and 50 mol % of MHM and HDP are completely suppressed. The activation energy \( E_a(\beta) \) and relaxation strength at -20 °C of the mixture \( \beta \) processes are provided in Table 6.2. To a first approximation, \( E_a(\beta) \) increases and \( \Delta \varepsilon \) decreases with number of hydroxyls per molecule with 10 mol % small molecules, excepting P2VPy/BPM. \( E_a(\beta) \) of P2VPy/10BPM does not display an increase with decreasing \( \Delta \varepsilon \), which perhaps due to a flexible carbon linkage between the two phenol groups (Figure 6.1). In addition, \( E_a(\beta) \) increases and \( \Delta \varepsilon \) decreases with increasing concentration of both DHN and BPM, but not for EPh. Therefore, the number of hydroxyls available for forming intermolecular linkages, the concentration of small molecules, and their structures play important effects on the energetics of pyridine rotation.
Figure 6.14. (a) Temperature dependence of the $\beta$ relaxation times of P2VPy and the mixtures of with EPh, BPM, DHN, MHM and HDP. Dotted lines indicate Arrhenius fits.
6.5 Dynamics of P2VPy/HDP Mixtures

6.5.1 Structural Evidence

FTIR results demonstrate that P2VPy/HDP exhibits an additional band at 3400 cm\(^{-1}\) due to hydrogen bonding as seen in Figure 6.3e. By comparing the spectra of neat EPh and neat HDP, the spectrum of the latter is found to display a distinct band at 3100 cm\(^{-1}\), which based on the chemistry involved in the P2VPy/HDP mixture, represents hydrogen bonding of either −C=O−H or −OH…O. For P2VPy/10HDP, multiple bands representing hydrogen bonding are convoluted in the region 3500 to 2800 cm\(^{-1}\). This includes a band at ~3400 cm\(^{-1}\) not found in neat HDP, the magnitude of which decreases

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_a(\beta)) [kJ/mol]</th>
<th>(\Delta\varepsilon(\beta)/[P2VPy]) At -20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2PVy</td>
<td>41</td>
<td>5.5</td>
</tr>
<tr>
<td>10 EPh</td>
<td>56</td>
<td>2.7</td>
</tr>
<tr>
<td>10 BPM</td>
<td>36</td>
<td>1.3</td>
</tr>
<tr>
<td>10 DHN</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>10 MHM</td>
<td>61</td>
<td>1.4</td>
</tr>
<tr>
<td>10 HDP</td>
<td>63</td>
<td>0.7</td>
</tr>
<tr>
<td>30 BPM</td>
<td>33</td>
<td>1.2</td>
</tr>
<tr>
<td>30 DHN</td>
<td>65</td>
<td>1.6</td>
</tr>
</tbody>
</table>
with increasing HDP content. It has been found previously that when both –H…N and –H–O are present, –H…N absorption appears at 3500-3300 cm\(^{-1}\) and the –H–O band appears at lower wavenumbers [44]. DSC results demonstrate that P2VPy with 10 mol % HDP has a much higher \(T_g\) than P2VPy mixed with 30 and 50 mol % HDP, confirming that the number of –OH…N bonds is highest in the 10 mol % HDP mixture. This suggests that at higher HDP contents, that HDP molecules form –H–O bonds between themselves rather than –OH…N formation with pyridine groups.

P2VPy/10HDP exhibits a small scattering peak at \(q \approx 0.06 \text{ Å}^{-1}\), which corresponds to a mean interdomain spacing of \(~10\text{ nm}\) (Figure 6.5a). Hydrogen-bonded mixtures possessing strong hydrogen bond linkages have been reported previously to exhibit SAXS peaks indicative of phase separation [23]. Based on DSC and FTIR results, P2VPy/10HDP perhaps exhibits phase separation due to the formation of a relatively large number of intermolecular hydrogen bonds. The upturn in scattering intensity at very small angles for the mixtures is due to spatial heterogeneity induced by the presence of hydrogen bond complexes [23].

Consistent with DSC observations, DMA results demonstrate that the mechanical \(\alpha\) relaxation of P2VPy/10HDP is located at a higher temperature relative to neat P2VPy (Figure 6.15). The presence of an extended rubbery plateau in \(E'\) suggests that P2VPy/10HDP imparts some physical crosslinking above \(T_g\) for this mixture. However no transitions above the \(\alpha\) relaxation are observed.
6.5.2 Dynamics of P2VPy/HDP using DRS

β process. Figure 6.12d shows that the β process P2VPy/10HDP mixtures is suppressed (β process of P2VPy mixed with 30 and 50 mol % of HDP is completely suppressed). Δε decreases compared to those of neat P2VP and other mixtures of P2VPy at 10 mol % (Table 6.2) due to a strong transient hydrogen bonding, restricting the rotation of pyridine groups.

α process. P2VPy mixed with 30 and 50 mol % of HDP display a similar segmental relaxation time behavior as does P2VPy mixed with EPh, BPM, DHN and MHM. P2VPy/10HDP relaxes much slower than neat P2VPy and the other mixtures (Figure 6.6e). The results are in accord with T_g behavior observed from DSC. The
segmental process is slightly broader than that of neat P2VPy, while those of mixtures containing 30 and 50 mol% are unchanged from neat P2VPy (Figure 6.7e).

**Figure 6.16.** The $\varepsilon''_{KK}$ spectrum vs frequency of P2VPy/10HDP at $T_g + 40 \, ^\circ\text{C}$. Inset: The $\varepsilon''_{KK}$ spectra vs frequency of P2VPy/10HDP at 150 -180 °C.

$\alpha_{MWS}$. Of the mixtures, P2VPy/10HDP is the only one to exhibit an additional process $\alpha_2$ at frequencies between $\alpha$ and $\alpha'$ (Figure 6.16). The $\alpha_2$ relaxation emerges from the $\alpha$ process at 160 °C and moves to higher frequency with increasing temperature (see the inset of Figure 6.16). As noted earlier, a slightly extended plateau in DMA and a very high $T_g$ suggest that P2VPy/10HDP contains strong intermolecular associations. At
first glance, it may seem reasonable to assign the $\alpha_2$ process to the association and
dissociation of a transient hydrogen bonded stickers ($\alpha^*$), as observed previously for
SPS-H (Chapter 3). A feature important to the $\alpha^*$ processes of SPS and in other H-
bonded systems that facilitates their assignment, is that $\Delta\varepsilon(\alpha^*)$ decreases with increasing
temperature, arising from the reduction the number of transient hydrogen bonded stickers
[25,27,45]. However, since $\Delta\varepsilon(\alpha_2)$ in fact increases with increasing temperature
(Figure 6.17), this process cannot be assigned to $\alpha^*$. Instead, based on the SAXS
scattering peak and by process of elimination, the $\alpha_2$ process is assigned to Maxwell-
Wagner-Sillars (MWS) interfacial polarization, arising from regions within the matrix
with markedly different dielectric constant and conductivity [46]. A similar process has
been previously observed in SPS7Zn ionomers (Chapter 4). The $\alpha_2$ relaxation emerges
from the $\alpha$ process at 160 °C and moves to higher frequency with increasing temperature
(see the inset of Figure 6.16). As noted earlier, a slightly extended plateau in DMA and a
very high $T_g$ suggest that P2VPy/10HDP contains strong intermolecular associations. At
first glance, it may seem reasonable to assign the $\alpha_2$ process to the association and
dissociation of a transient hydrogen bonded stickers ($\alpha^*$), as observed previously for
SPS-H (Chapter 3). A feature important to the $\alpha^*$ processes of SPS and in other H-
bonded systems that facilitates their assignment, is that $\Delta\varepsilon(\alpha^*)$ decreases with increasing
temperature, arising from the reduction the number of transient hydrogen bonded stickers
Figure 6.17. Dielectric strengths for the $\alpha$ and $\alpha_2$ processes of P2VPy/10HDP as a function of temperature.
6.6 Summary

In all mixtures except P2VPy/10HDP, DSC $T_g$s matched reasonably well with predictions of the Fox equation. WAXD results indicate only the two amorphous halos of P2VPy, with no crystallinity or clusters. In all mixtures, broad FTIR bands between 3000 cm$^{-1}$ and 3500 cm$^{-1}$ are present, indicating significant intermolecular $-$OH$\cdots$O and $-$OH$\cdots$N bonding. These bands generally increase in intensity with small molecule concentration.

High-temperature DRS found two processes, the $\alpha$ process and $\alpha'$ process, the latter attributed to electrode polarization. The significant broadened $\alpha$ relaxation time distribution of P2VPy mixed with BPM, DHN and MHM at 30 and 50 mol % is attributed to dynamic heterogeneity, whereas P2VPy/EPh mixtures exhibit dynamic homogeneity.

P2VPy exhibits a strong and broad local relaxation due to the rotation of pyridine side-groups. $\varepsilon(\beta)$ was suppressed in P2VPy/10EPh due to a reduction in the local free volume, restricting the rotation of pyridine groups. For all other mixtures, the presence of small molecules with multiple hydroxyls suppressed the $\beta$ process due to the formation of transient crosslink leading to a decrease in the number of remaining free pyridine groups, or the reduction of local free volumes. In addition, the relaxation strength $\Delta\varepsilon(\beta)$ decreased and activation energy $E_a(\beta)$ increased with increasing number of hydroxyl groups per molecule.

P2VPy/10HDP was the only mixture that formed a strong intermolecular hydrogen-bonded complex. It had a significantly higher $T_g$ and $T_{ref}$ and exhibited a small
scattering peak in SAXS. Also, an additional $\alpha_2$ process was found at higher temperatures, which was assigned to an MWS relaxation, consistent with the existence of phase-separated complexes within the P2VPy matrix.

6.7 References


34. Coleman, M.M.; Graf, J.F; Painter, P.C. *Specific interactions and the miscibility of polymer blends*; Technomic Publishing: PA, **1991**.


Chapter 7

Summary and Suggestions for Future Work

7.1 Summary

Broadband dielectric spectroscopy was the primary experimental tool used to investigate the dynamics of ion-containing and intermolecular hydrogen-bonded polymers. The systems under consideration included SPS copolymers, SPS ionomers, P2VPy - LiClO$_4$ mixtures, and solutions of P2VPy with low molecular weight phenolic molecules. Intermolecular coupling, through either ionic or hydrogen bonding, was found to strongly impact the local $\beta$ relaxation of the host polymer by inhibiting motion of the sulfonic phenyl groups in SPS ionomers, and the pyridine pendant groups in P2VPy mixtures and solutions. The $\beta$ relaxation strength in the ionomers was suppressed by ionic interactions, which act as transient physical crosslinks, while suppression of the $\beta$ relaxation of P2VPy – LiClO$_4$ mixtures resulted from either the formation of transient crosslinks leading to a subsequent decrease in the number of free pyridine groups or the reduction in the local free volume in the presence of LiClO$_4$. Suppression of the $\beta$ process in P2VPy solutions was observed in the presence of small phenolic molecules possessing multiple hydroxyls, primarily due to the formation of transient intermolecular hydrogen bonding. However, suppression of the $\beta$ process in P2VPy mixed with 10 mol % EPh, a single-hydroxyl small molecule, is more likely due to the reduction of local free volumes in the presence of EPh molecules.
The observation of additional processes at temperatures above the segmental $\alpha$ relaxation was achieved using a numerical version of the Kramers-Kronig transform. Relaxations associated with Maxwell-Wagner-Sillars interfacial polarization and electrode polarization were found in the dielectric spectra of SPS ionomers, while for SPS-H two relaxations were observed and attributed to hydrogen bond association/dissociation and electrode polarization.

Three relaxations above the segmental relaxation were observed in P2VPy - LiClO$_4$ mixtures and attributed to the predominant segmental relaxation, ion-mode relaxation, slow hindered segmental relaxation and electrode polarization. Above the segmental process only electrode polarization was observed for P2VPy solutions except for P2VPy/10HDP. P2VPy/10HDP also exhibited an additional process, attributed to MWS polarization arising from the presence of phase-separated complexes within the P2VPy matrix.

Results from DSC, FTIR, DMA, SAXS and WAXD were very important in interpretation of DRS spectra. DSC exhibited a single $T_g$ for SPS copolymers, SPS ionomers, P2VPy - LiClO$_4$ mixtures and P2VPy solutions. Slightly increases in $T_g$s for SPS copolymers and ionomers were observed relative to neat PS. Increases in the $T_g$s of the P2VPy – salt mixtures with increasing LiClO$_4$ concentration suggested an increase in the number of Li$^+\cdots$N interactions. $T_g$s of P2VPy solutions matched reasonably well with prediction of the fox equation except for P2VPy/10HDP. This solution displayed an extremely high $T_g$ than neat P2VPy and neat HDP.

FTIR was used to establish the conformational state of sulfonic acid and ionic species as well as the degree of intermolecular hydrogen bonding. DMA and SAXS
assisted in determining the morphology of ion-containing polymers and hydrogen-bonded systems. DMA experiments indicated phase separation in SPS ionomers, which was absent in the SPS copolymers, P2VPy - LiClO₄ mixtures and most P2VPy solutions. Only SPS7Zn and P2VPy/10HDP exhibited a scattering peak in SAXS. Moreover, no crystalline peaks were observed using WAXD, indicating excellent dispersion of small molecules in the polymer matrix for P2VPy mixtures and solutions and no residual metal hydroxide in the SPS ionomers.

As the preceding chapters have illustrated, intermolecular hydrogen-bonded and ion-containing possess an extremely complex collection of dynamical relaxations. The work presented in this thesis goes further than any previous study to quantify these dielectric relaxations and assign them to their microscopic or macroscopic origins, especially in light of the data obtained from complementary techniques. Future studies of dielectric relaxations in hydrogen-bonded or ion-containing polymers will greatly benefit from the assignments made in this thesis.

7.2 Suggestions for Future Work

In this thesis DRS was used to elucidate the dynamics in several ion-containing and hydrogen-bonded polymer systems at the segmental and local levels. However, further improvements in the quantitative understanding of the dynamics and structural features are possible. As described in Chapter 4, the assignment of MWS polarization in ionomers was based on the observation of a SAXS scattering peak for SPS7Zn and previous studies that found two phases in SPS7Na and SPS7Cs. A more quantitative
description of phase separation due to ionic clusters can be obtained by using high voltage DRS. The measurement of the non-linear response of the dielectric constant as a function of dc bias field can provide a measure of the ion cluster size. This method has been established in ceramic ferroelectrics by using the modified Devonshire-Langevin relation [1]:

\[ \varepsilon'(E) = \varepsilon'_1 - \varepsilon'_2 E^2 + \varepsilon'_3 E^4 + \left( \frac{P_r \varepsilon}{\varepsilon_0} \right)[\cosh(E \zeta)]^{-2} \]  

(7.1)

where \( E \) is the magnitude of the electric field, \( P_r \) is the effective polarization of one cluster, \( \zeta = \frac{P_r L^3}{2k_B T} \), and \( L \) is the cluster size. Not only can the cluster size be measured by this relation but also the polarization of the cluster.

Although the broad picture of the dynamics of the cations in P2VPy - LiClO₄ mixtures was revealed here by DRS (Chapter 5), the precise details of the complicated molecular dynamics need further clarification. There is a general lack of understanding of cation and anion diffusion in polymeric systems. Additional insight would be gained by considering salts with different anion sizes. LiClO₄, studied here, is a medium size anion, whereas larger anions include poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide) lithium (LiPPI) and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) (Figure 7.1). Since large anions diffuse more slowly and tend to promote dissociation of ion pairs, more free cations will be available to coordinate with the polymer [2,3]. This assists study of the contribution of the cation to conductivity and, by comparison between systems, will help to separate the impact of the cation and anion.
7.3 References


VITA

Pornpen Atorngitjawat

Pornpen ‘Noi’ Atorngitjawat was born in Chonburi, Thailand. While studying high school at Chonkunyanukoon in Chonburi, she became interested in science. After finishing high school, she joined the Department of Science at Chulalongkorn University in Bangkok. She obtained both her B.S. and M.S. degrees in Materials Science from Chulalongkorn University, with a full scholarship from the National Science and Technology Development Agency (NSTDA) during her Masters work. After six years in a happy-pink house, she joined the faculty at the Department of Materials Science and Gemology at Burapha University in Chonburi, Thailand. In Fall 2002, she was granted a full scholarship from the Royal Thai Government to pursue a PhD at the Pennsylvania State University, specifically in the Department of Materials Science and Engineering (Polymer Science program) under Professor James Runt. After almost five years at Penn State, she is returning to work at Burapha University in Chonburi.