Synthesis and Electrical Properties of Functional Block Copolymer/Inorganic Nanocomposite Materials

Hongying Chen
University of Southern Mississippi

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SYNTHESIS AND ELECTRICAL PROPERTIES OF FUNCTIONAL BLOCK COPOLYMER/INORGANIC NANOCOMPOSITE MATERIALS

by

Hongying Chen

Abstract of a Dissertation Submitted to the Graduate School of The University of Southern Mississippi in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2010
ABSTRACT

SYNTHESIS AND ELECTRICAL PROPERTIES OF FUNCTIONAL BLOCK COPOLYMER/INORGANIC NANOCOMPOSITE MATERIALS

by

Hongying Chen

December 2010

Sulfonated poly[styrene-b-ethylene-co-butylene-b-styrene] (sSEBS) block copolymers/inorganic nanocomposite materials were synthesized via in situ formation of inorganic fillers and characterized particularly for their dielectric properties and proton conductivities.

In preparation of sSEBS/SrTiO$_3$ nanocomposites, titanium (IV) isopropoxide [Ti(OPr)$_4$] complex was diffused into sSEBS film, followed by subsequent hydrolysis of [Ti(OPr)$_4$], diffusion of strontium cations in sSEBS domains, and in situ formation of crystalline SrTiO$_3$. sSEBS with sulfonation degree of 38.1% and 65.0% were employed, and relevant sSEBS/SrTiO$_3$ composites contain SrTiO$_3$ of 10-15 wt%. Elemental composition characterization with ESEM/EDX indicated uniform distribution of Sr and Ti. TEM images revealed clusters of SrTiO$_3$ rods were selectively formed in hydrophilic domains in sSEBS with nanophase separation in lamellar morphology. TEM/SAED of sSEBS/SrTiO$_3$ confirmed crystalline SrTiO$_3$ structure inside composite film. The dielectric enhancement and shift with frequency showed potential of these materials for energy storage and conversion devices.
sSEBS/silicate composites as model nanocomposite proton exchange membranes were prepared via in situ sol-gel reactions of tetraethylorthosilicate (TEOS) in sSEBS solutions that were solution cast into films. These hybrid membranes exhibited nanophase separated morphology with the particles mainly dispersed in the hydrophilic sulfonated block. The number of water molecules per sulfonic acid group increased with silicate content. Some sSEBS/silicate membranes exhibited lower methanol permeability than Nafion® 117 while others showed higher methanol permeability. Methanol permeability increased with introduction of silicate which was attributed to the broadening of hydrophilic domains by silicate insertion. Besides mechanical improvement, proton conductivity increase in membranes containing around 10wt% silicate is discussed in terms of the morphological change and synergetic effect by silicate particles.

Macromolecular dynamics of sSEBSs were investigated using broadband dielectric spectroscopy (BDS). Two main relaxations corresponding to the glass transitions in the EB and S block phases were identified, and their temperature dependences were VFT - like. $T_g$ for the S block phase shifted to higher temperature due to restrictions on chain mobility caused by hydrogen bonded SO$_3$H groups. While the EB block phase $T_g$ appeared to remain constant with degree of sulfonation in DMA experiments, it shifted somewhat upward in BDS spectra. The fragilities of the EB and S block domains in sSEBS decreased after sulfonation. The temperature dependence of the dc conduction contribution to sSEBS loss spectra also followed VFT-like behavior, and S block segmental relaxation time correlated well with conductivity according to the fractional Debye-Stokes-Einstein equation.
The University of Southern Mississippi

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CHAPTER I
INTRODUCTION TO POLYMER/INORGANIC NANO COMPOSITE MATERIALS

Polymer/Inorganic Nanocomposites

Polymer/inorganic nanocomposites represent a class of materials composed of a host polymer matrix in which inorganic inclusions are dispersed throughout. Unlike conventional composite materials, which include fillers on a micrometer scale, nanocomposites contain fillers with characteristic nanometer length scales, usually from 1 to 100 nm. The properties of polymer-inorganic nanocomposites depend on the properties of the constituent materials, length scale, as well as chemical composition and morphological details of particle dispersion. Through synergistic combination of polymer matrix and included fillers, polymer-inorganic nanocomposites may enhance and improve mechanical, optical, electrical or other important properties. In past decades, much research interest has been shown in improving mechanical properties in polymer-inorganic nanocomposites, a successful example of which is polymer-clay systems. Research activities in the area of polymer-inorganic nanocomposites have expanded to include a wide variety of applications such as nanocomposite membranes for gas separation, proton exchange membranes for fuel cells and as well as from nanodielectrics in the electrical power industry to supercapacitor materials. In the subsequent section, polymer nanocomposites within the context of membranes for fuel cells will be reviewed briefly.

Polymer/Inorganic Nanocomposites as Polymer Electrolyte Membranes

Polymer electrolyte membrane fuel cells (PEMFCs) have been developed mainly for applications in the automotive, portable and stationary power areas. As an electrochemical device that converts chemical energy in fuels into electrical energy directly, a PEMFC uses hydrogen or methanol as fuel and conducts electrochemical
reactions at the anode and cathode to generate an electric current that energizes an external load. Membrane electrolyte assemblies (MEAs) are the essential part in a PEMFC, which mainly consists of two electrodes and a polymer electrolyte membrane sandwiched between anode and cathode (Figure I-1).

![Figure I-1. Basic membrane electrolyte assembly.](image)

The polymer electrolyte membranes (also termed “proton exchange membranes”) (PEMs), used as the proton conductor and fuel separator in PEMFCs, play an important role in the operation of PEMFCs. The search for new types of polymer electrolyte membranes has continued to be an active area of research in order to improve the performance of PEFC and enable the commercialization of PEMFCs. Ideally, PEMs should have high proton conductivity, low permeability to fuels that must remain separated, no electronic conductivity, excellent electrochemical stability towards hydrolysis, oxidation and reduction, and good mechanical properties.

Nafion is currently the benchmark material in PEM research. Its poly(perfluorosulfonic acid) structure provides exceptional oxidative and chemical stability and the unique morphology of interconnected ionic clusters in the
semicrystalline perfluorinated matrix imparts good proton conductivity and mechanical properties. Nafion membranes show good performance under certain conditions but have certain serious problems that remain unresolved.\textsuperscript{15,19,20} Firstly, Nafion is expensive for commercialization on a large scale. Secondly, Nafion is limited to operation below 80 °C due to conductivity loss caused by dehydration. Thirdly, for direct methanol fuel cell (DMFC) applications, the excessive methanol crossover limits the fuel efficiency. These disadvantages have encouraged extensive studies of alternative PEM materials, including poly(arylene ether)s, poly(amide)s,\textsuperscript{21} polyphosphazenes and polymer based hybrid materials.\textsuperscript{22,23,24}

Study of structure and property relationship is an important subject in the design and development of novel PEM materials with good performance. It was found that microstructure and morphology have great influence on water uptake, permeability, and proton conductivity. For example, Nafion membranes exhibit higher proton conductivity than most alternative polymers with similar ion exchange capacity (IEC). In Nafion membranes, sulfonic acid groups aggregate into ionic domains in the semicrystalline matrix. Upon hydration, ionic groups expand with increasing water uptake and connect with each other to form a network of ionic channels when the water content reaches the percolation concentration threshold.\textsuperscript{25} These morphological characteristics of Nafion are responsible for its excellent conductivity in the comparative study with sulfonated poly(ether-ketone) (PEEKK) membranes.\textsuperscript{26}

Block copolymers are known for their ability to self-assemble into nanophase separated morphologies due to the contrast in the chemical nature of the two blocks.\textsuperscript{27} Ghassemi et al. reported the synthesis of multiblock copolymers consisted of sulfonated
poy(arylene ether sulfone) (PAES) and fluorinated poly(arylene ether) blocks, which exhibited well defined phase separation and well connected hydrophilic domains, while random sulfonated PAES and Nafion N112 exhibited isolated ionic domains in TM-AFM phase images. Lee also reported similar multiblock copolymers that possessed higher proton conductivity than random sulfonated PAES with similar ion exchange capacity (IEC). Graft copolymers are a class of nonlinear block copolymers. By adjusting the length and the number density of graft chains, a huge potential exists for controlling morphology. In Ding’s study of polystyrene-g-macromonomer polystyrenesulfonic acid (PS-g-macPSSA), the graft copolymers exhibited 3-5 times larger conductivity (0.24 S/cm) than Nafion 117 at similar water uptake owing to evident ionic aggregates and continuous ionic networks.

Among development of novel materials for PEMs, polymer composite membranes have attracted considerable attention. In facing the challenges of high performance, high chemical and physical durability, affordable cost, operation at high temperature, and reduction of fuel permeation, polymer composites have shown good potential for improvement in various properties. In the study and development of polymer composites as PEMs, the polymer component provides mechanical strength and proton conductivity while the inorganic phase is expected to reduce fuel permeation (i.e., of methanol or hydrogen) and improve both thermal and chemical stability. Most of these materials belong in the realm of nanocomposites since most of them have inorganic inclusions on the nanometer scale. Based on the nature of the polymer and the inorganic inclusions, the considerable number of polymer nanocomposites for PEMs that have been studied including montmorillonite (MMT), SiO₂, ZrO₂, zeolites and zirconium.
phosphate fillers,\textsuperscript{40} and Nafion,\textsuperscript{41} sulfonated polyetheretherketone (sPEEK),\textsuperscript{42} sulfonated polysulfone (sPSF),\textsuperscript{43} sulfonated polybenzimidazole (PBI)\textsuperscript{44} polymers.

As we discussed, morphology is an important influence on membrane properties. In particular, block copolymers have shown improvement in properties resulting mainly from well controlled morphology that structures proton conducting pathways. However, there has not been much research in block copolymer nanocomposites for PEMs, and little attention has been given to the study of morphology and property relationship in this class of nanocomposites. This will be the subject of part of the work presented in this dissertation.

Preparation of Polymer/Inorganic Nanocomposites

The nanocomposite preparation process will influence its structural evolution, which will influence final properties. Currently, various synthesis approaches have been employed in preparation of polymer-inorganic nanocomposites, owing to the ability to combine polymer and inorganic phases in different ways.\textsuperscript{45} With regard to the inorganic particles, they can be synthesized in situ during the process, or ex situ synthesized particles introduced into the polymer. Similarly, introduction of polymers into nanocomposites can be realized through two different ways: in situ polymerization of monomers or utilizing polymers directly. The combination of in situ and ex situ synthesis of inorganic particles and polymer matrix will generate four types of strategies for the preparation of nanocomposites, as illustrated in Figure I-2.
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</table>

**Figure I-2.** Four types of strategies for preparation of nanocomposites.

In strategy A, the mixing of polymers and inorganic nanoparticles can be conducted by blending nanoparticles in polymer solutions or by compounding into a polymer melt.\textsuperscript{46,47,48,49,50} To facilitate good dispersion in the polymer matrix, the inorganic nanoparticles may undergo surface-treatment to improve compatibility between two phases before incorporation into polymers. Another tactic to improve compatibility is addition of coupling agents. In strategy B, nanocomposites can be prepared through two ways: (A) in situ synthesis of nanoparticles in preformed polymer films, and (B) solution casting (or co-assembly) from multi-component solutions of inorganic precursor and polymer.\textsuperscript{51} In the first approach in strategy B, the inorganic precursor molecule permeates into a preformed polymer film and subsequent reaction of precursors results in the formation of nanoparticles in targeted polymer domains. The interaction between the inorganic precursor molecules and polymer film template may influence the particle size and distribution throughout the polymer matrix. In the second approach of solution casting from multi-component solutions, polymers and inorganic precursor molecules are mixed in solvent to form miscible multi-component solutions, and the nanocomposites result from solution casting and evaporation of the solvent during controlled drying. The
polymerization of inorganic precursors proceeds in initial polymer solution and continues during the formation of nanocomposites driven by the evaporation of solvent. During the drying process, the co-assembly of inorganic inclusions and polymer blocks will contribute to the particle dispersion and morphology of nanocomposites. In strategy C, ex situ formed inorganic particles are dispersed in organic monomers where interactions between monomers and particles may help the dispersion of particles. Polymerization of the organic monomers will form the polymer matrix, followed by solution casting. In strategy D, inorganic precursors are mixed with organic monomers; the in situ synthesis of inorganic particles and polymerization of organic monomers proceeds simultaneously.

Sometimes the term “hybrid materials” is used in the context of polymer-inorganic composite materials. The most wide-ranging definition of a hybrid material refers to having two moieties blended on the molecular scale. There is a gradual transition between hybrid materials and nanocomposites, while the latter has at least one component on a nanometer level. Commonly, hybrid is more often used if the inorganic units are formed in situ by molecular precursors, for example through sol-gel reactions.

In this research, the two synthesis routes in Strategy B will be employed to prepare polymer-inorganic nanocomposites. In following section, a general overview of synthesis of inorganic nanoparticles will be described.

**Preparation of Inorganic Nanoparticles**

Inorganic nanoparticles can be synthesized by different techniques, such as co-precipitation, sol-gel processing, hydrothermal/solvothermal and other methods. For preparation of nanocomposites via polymer in situ synthesis of inorganic precursor
molecules, the synthesis in the polymer environment is critical because it will determine the final particle size and dispersion in the matrix. The reactions of inorganic nanoparticle precursors in the presence of a polymer, or organic monomers, will proceed somewhat differently than if these reactions occurred in a homogeneous, essentially neutral medium due to interactions between inorganic and organic units. Nonetheless, it is helpful to understand the basic reaction mechanism of inorganic precursors in the absence of polymer solutions or polymer film templates. Particularly, a general introduction will be given to sol-gel and sol-precipitation methods because these methods were utilized to prepare the nanocomposites in this research.

Preparation of Silicate Particles via Sol-Gel Reactions

The sol-gel process is a versatile and relatively simple method that can produce various types of metallic, inorganic, organic, and hybrid materials.\textsuperscript{56,57} Meanwhile, it is also an important method to prepare advanced functional materials having optical, electrical and magnetic properties owing to the broad choice of sol-gel precursor molecules (metal alkoxides) and flexible processing conditions.\textsuperscript{58,59,60} The sol-gel process has also been widely utilized to prepare nanoparticles and polymer-inorganic nanocomposites.\textsuperscript{61}

This process consists of the evolution of inorganic oxide networks through the initial formation of colloidal suspensions (sol state) and subsequent gelation of the sol to form networks (gel state) in a continuous liquid phase. Metal alkoxides (M[OR]\textsubscript{n}, M = Si, Al, Ti, etc.) are the common precursors that are used and are sensitive to moisture. Hydrolysis of metal alkoxides and polycondensation are the basic sol-gel reactions.\textsuperscript{62} Silicon alkoxides are one type of the most widely studied sol-gel precursors. Their
reactions in sol-gel process are illustrated in Figure I-3. In equation 1, one alkoxy group is substituted by a hydroxyl group after hydrolysis. Equations 2a and 2b show the formation of Si-O-Si chains due to condensation between two hydrated silicon alkoxides or condensation of hydrated silicon alkoxide with unhydrated silicon alkoxide. In a conventional sol-gel process in a homogeneous liquid, for the preparation of ceramic thin film products, gelation will result in a dramatic increase in the viscosity of the solution after the formation of an oxide- or alcohol-bridged network via sufficient polycondensation.

**Figure I-3.** Scheme of silicon alkoxide sol-gel reaction.  

It is essential to understand the kinetics of hydrolysis and condensation reactions as the ratio of their rate constants ($k_H/k_C$), will determine the structure and morphology of the final product structures. Parameters that influence the sol-gel reaction include reactivity of alkoxides, organic moiety (OR groups), ratio of H$_2$O/alkoxide, pH, reaction temperature and solvent type. In comparison to hydrolysis of Si(OR)$_4$, the hydrolysis of other metal alkoxides M(OR)$_n$ (M = Al, Ba, Ti, Zn, etc.) is extremely rapid. With regard to alkoxy groups, a general rule is that the longer and the bulkier they are, the slower is the hydrolysis rate. The increase of H$_2$O/alkoxide ratio and temperature tends to increase the rate constant. Artaki et al. suggested, with the aid of NMR analysis that $k_H$
increases in the sequence of acetonitrile, methanol, dimethylformamide, dioxane and formamide, with the $k_H$ of acetonitrile being about 20 times larger than that of formamide.\textsuperscript{68}

pH (controlled by addition of acids: HCl or HNO$_3$; or alkali: NH$_3$ or NaOH) is an important factor that can be used to regulate the rates of hydrolysis and condensation.\textsuperscript{69,70,71} Hydrolysis of Si(OR)$_4$ follows a nucleophilic substitution (S$_N$2) mechanism in the presence of either acid or basic catalyst, characterized by the pentacoordinate transition state of Si. The degree of hydrolysis of metal alkoxides strongly affects the structure of Si-O-Si network. Since OH$^-$ is a marginally better leaving group than –OR, water condensation (Equation 2a) proceeds more quickly than alcohol condensation (Equation 2b). Therefore, pH influences the condensation reaction significantly. In acidic catalysis, the formation of Si-O-Si chains undergoes the protonation of -OR (or -OH) in Si(OR)$_{4-n}$(OH)$_n$, formation of pentacoordinate transition state of Si, and elimination of the ROH or H$_2$O molecules. Under basic catalysis, activation of condensation occurs via formation of highly nucleophilic fragments such as Si(OH)$_3$O$^-$, which attacks the positively charged Si in Si(OR)$_{4-n}$(OH)$_n$. Si-O-Si, followed by formation of Si-O-Si networks with the elimination of OH$^-$ groups. The choice of acid or base catalyst has an important influence on the microstructure of the resulting gel network or particles. Under acidic conditions (pH < 4), the rate of hydrolysis will be higher than the rate of condensation, and the rate of condensation decreases with the degree of hydrolysis (n in the formula Si[OR]$_{4-n}$[OH]$_n$). Consequently, Si-O-Si chains tend to preferentially form in the early stages of the polymerization process, followed by subsequent branching and cross-linking of the chains. Under basic conditions, the
stability of transition states in the formation of Si-O-Si links increase with the degree of hydrolysis ($n$). Thus, the rate of condensation also increases with $n$. Although many factors may affect the microstructure of the final gel network, the general trend is that acid-catalyzed reactions will yield primarily linear or randomly branched networks while base-catalyzed reactions will yield highly branched clusters which do not interpenetrate prior to gelation and thus behave as discrete clusters. The effect of pH value on microstructure evolution is illustrated in Figure I-4.

![Figure I-4. Effect of pH on particle morphology in sol-gel reactions.](image)

**Figure I-4.** Effect of pH on particle morphology in sol-gel reactions.\(^{72}\)

*Preparation of Barium Titanate (BaTiO\(_3\)) and Strontium Titanate (SrTiO\(_3\)) Nanoparticles via Sol-Precipitation Method*

Complex metal oxides such as SrTiO\(_3\), BaTiO\(_3\), Pb(Zr, Ti)O\(_3\) and (Ba,Sr)TiO\(_3\) have extensive applications in transducers, actuators, and high-k dielectrics due to their ferroelectricity.\(^{73,74}\) Ferroelectricity refers to the phenomenon in which materials exhibit spontaneous polarization and a hysteresis effect with respect to the dielectric displacement in the presence of an applied electric field. Ferroelectricity in metal oxides arises from the special crystal structure in these materials.
The preparation of BaTiO\textsubscript{3} and SrTiO\textsubscript{3} (MTiO\textsubscript{3}, M = Ba or Sr) nanoparticles can be classified into two high temperature and low temperature syntheses. In the high temperature approach, MTiO\textsubscript{3} nanoparticles are prepared through conventional ceramic means involving mechanical mixing of MO or MCO\textsubscript{3} (M = Ba or Sr) and TiO\textsubscript{2} that occurs along with progressive thermal treatment. Temperatures > 1000 °C are usually needed in order to facilitate the diffusion of metal cations to form ordered crystal structures.\textsuperscript{75,76} The low temperature synthesis methods refers to the preparation of MTiO\textsubscript{3} nanoparticles in a liquid phase at low temperatures (≤ 100 °C), including a sol-gel,\textsuperscript{77,78} hydrothermal,\textsuperscript{79,80} and sol-precipitation (or alkoxide-hydroxide route) methods.\textsuperscript{81,82}

The sol-gel method starts with the preparation of precursor solutions of titanium alkoxide and barium alkoxide (or strontium alkoxide) in alcohol, followed by hydrolysis of these precursors via addition of water and further aging of hydrolyzed products to allow the gelation and condensation reactions. The hydrothermal method usually proceeds at temperatures over 100 °C, while the sol-precipitation method takes place at temperatures lower than 100 °C. Among the preparation methods at low temperature, the sol-precipitation method has gained interest in recent years because it provides more space to regulate the particle size and paves the way for preparation of submicron uniform species.\textsuperscript{83,84,85,86}

There is no essential difference in the reaction mechanism between hydrothermal method and sol-precipitation method.\textsuperscript{87} The widely accepted reaction mechanism for sol-precipitation is illustrated in the equations below.\textsuperscript{88,89,90}

\[
\text{Ti(OR)}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2 \text{(gel)} + 4 \text{ROH} \quad \text{Eq. 1}
\]
\[
\text{TiO}_2 \text{(gel)} + \text{M(OH)}_2 \rightarrow \text{MTiO}_3 + \text{H}_2\text{O} \quad \text{Eq. 2}
\]
In the sol-precipitation process for preparation of MTiO$_3$, the hydrolysis and condensation reactions of Ti(OR)$_4$ result in the formation of a gel of hydrated titanium oxide, after which aqueous M(OH)$_2$ solution is added to the reaction system of Ti(OR)$_4$ precipitates, followed by the diffusion of M$^{2+}$ cations into the TiO$_2$ gel followed by the formation of crystalline MTiO$_3$ with condensation. In a more widely used way, the barium (or strontium) salt (such as BaCl$_2$ or Sr[NO$_3$]$_2$) and strong base (such as NaOH or KOH) are added to the reaction system of Ti(OR)$_4$ hydrolysis products in sequence, instead of addition of M(OH)$_2$ directly.$^{91,92}$

To better control the process, it is necessary to understand the factors that influence the evolution of crystalline structure, particle size and morphology. In the study by Diaz-Guemes et al., a strong alkaline environment was seen to be essential for the formation of crystalline MTiO$_3$. In their study, crystalline BaTiO$_3$ was obtained only when pH $>$ 11.$^{88}$ It was suggested that the absorption of (OH)$^-$ groups into TiO$_2$ gel particles generated negative particles, which made it easier for metal cations to diffuse inside the particles to counterbalance the negative charge. Diaz-Guemes also concluded from his research that the particle size was determined mainly by the characteristic of the TiO$_2$ gel initially formed. However, Golubko et al. did not find the relation between TiO$_2$ gel and final MTiO$_3$ particle size.$^{93}$ They concluded that the rate of absorption of barium or strontium cations by the product of the hydrolysis of Ti(OBu)$_4$ is the main factor that determines the morphology of perovskite species MTiO$_3$. Size and particle uniformity of the complex oxide decreases drastically with increase of the absorption rate. The absorption rate of M(OH)$_2$ (M = Ba, Sr) increases with increase in temperature and concentration of the hydroxide solution, and Sr(OH)$_2$ is absorbed much more readily than
Ba(OH)$_2$. It was found that SrTiO$_3$ can be prepared at lower temperatures and shorter reaction times under which BaTiO$_3$ could not be prepared. This difference in adsorption of Sr(OH)$_2$ and Ba(OH)$_2$ is a reasonable explanation for the easier synthesis of crystalline SrTiO$_3$ than BaTiO$_3$. Although the TiO$_2$ gel might be not a significant factor to determine the final particle size of MTiO$_3$, the hydrolysis product of Ti(OR)$_4$ is important in the preparation process. For example, aging of Ti(OBu)$_4$ resulted in essential reduction of the reaction rate or did not produce perovskite crystallization at 85 °C.\textsuperscript{93}

Ti(OR)$_4$ hydrolysis usually proceeds very fast due to its high reactivity. This rapid hydrolysis may reduce the reactivity of the hydrolyzed TiO$_2$ gel.\textsuperscript{94} Therefore, chelating agents (such as acetic acid or acetylacetone) have often been used to control the hydrolysis and condensation reactions.\textsuperscript{95,96,97} The reaction of acetylacetone (acacH) with Ti(OR)$_4$ is illustrated the equation below in which –OR groups are partially substituted by a chelating moiety depending on the molar ratio.

\begin{equation}
\text{Ti(OR)$_4$ + x (acacH) $\rightarrow$ Ti(OR)$_{4-x}$(acac)$_x$ + x ROH} \quad \text{Eq. 3}
\end{equation}

The titanium complex with acetylacetone is relatively stable even in the presence of a large excess of water. The structure of the Ti(OR)$_4$ complex is dependent on the ratio of acetylacetone and Ti(OR)$_4$, usually in the range of 1 ~ 4 or higher. Léaustic et al. investigated the complex of Ti(OR)$_4$ (OR = OPr$^i$, OEt) and acetylacetone with molar ratio of 1, in which the structure of Ti(OR)$_3$(acac) was identified.\textsuperscript{98,99} Hung et al. studied the optimization with experimental statistical method in the synthesis of BaTiO$_3$ nanoparticles using acetylacetone as chelating agent in a sol-precipitation process.\textsuperscript{100} BaTiO$_3$ nanoparticles with average size of 50 nm were prepared using the optimized parameters: (A) the molar ratio of water to Ti(OPr$^i$)$_4$ was 15, (B) the molar ratio of
acetylacetone to Ti(OPr\(^i\))\(_4\) was 4, (C) the KOH concentration was 5M, (D) the agitation speed was 465 rpm, and (E) the reaction temperature was 100 °C.

Polymer-Inorganic Nanocomposites via In Situ Synthesis Approaches

Mauritz and coworkers have conducted extensive research in the preparation of a number of nanocomposites using the two approaches in strategy B as described previously. With the method of in situ synthesis in preformed polymer films, they prepared Nafion/silicate (Nafion is a DuPont perfluorosulfonate ionomer),\(^{101,102}\) Nafion/zirconia,\(^{103}\) poly(n-butyl methacrylate)/titania,\(^{104}\) polyethersulfone/silica,\(^{105}\) Surlyn/titania (Surlyn is a DuPont poly[ethylene/methacrylic acid]),\(^{106}\) poly(styrene-b-isobutylene-b-styrene) ionomer/silicate\(^{107,108}\) and sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene]/CoFeO\(_4\).\(^{109,110}\) Lee et al. explored the in situ synthesis of crystalline BaTiO\(_3\) particles in a hydroxylated poly(styrene-b-butadiene-b-styrene) thin film template.\(^{111,112}\)

The typical procedure for this method is as follows. A preformed polymer film, prepared by solution casting or melt pressing, is immersed in an organic solvent to allow for sufficient swelling that will allow permeation of reactants. Then, the swollen polymer film is transferred to a solution of inorganic precursors. The polymers used in this method usually contain functional groups like SO\(_3\)H or COOH. Due to the chemical affinity between the functional groups and inorganic precursors, the precursors will selectively diffuse into the targeted domains (of functional groups) in the swollen polymer film. Block copolymers containing hydrophilic blocks will have nanophase separated morphologies consisting of hydrophobic and hydrophilic domains. Therefore, when block copolymer films are employed, the precursors selectively migrate into the hydrophilic
domains, and inorganic nanoparticles are formed within these regions via condensation or precipitation reactions. After the reactions, the polymer film is washed to remove residues on the surface and dried to remove solvent. The particle size and dispersion in the film is controlled by the polymer morphology which acts as a template. Since phase separation in block copolymers is at the nanometer level (~20 nm), this method is an effective way to prepare nanocomposites. The polymer template morphology as well as concentration of functional groups may influence the final loading and dispersion of inorganic particles because it may determine the absorbance of inorganic precursors.

Mauritz and coworkers also studied preparation of nanocomposites, including sSEBS/silicate, polyethersulfone/silica, and poly[styrene-b-maleated (ethylene-co-butylene)-b-styrene]/silicate, using the second approach in strategy B, solution casting of multi-component solution. Other nanocomposites prepared with this method include sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene]/TiO$_2$ and polymethyl meth-acrylate/silica. In this approach, polymer and inorganic precursors is mixed in solution. The reaction of precursors will be influenced by the dissolved polymer chains. The polymer may react with precursor like chelating agent, or attach to the surface of particles formed in solution. After solution casting, the evaporation of solvent will induce cooperative self-assembly of polymer chains and inorganic particles during the drying process. The interaction between the chains in the polymer environment and inorganic particles will influence the final particle dispersion and morphology of the resultant nanocomposite. One advantage of this method is the wide range of inorganic loading in nanocomposites as long as the precursors dissolve well in the multi-component reactive solution.
In this research, two types of nanocomposites, sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene]/strontium titanate (sSEBS/SrTiO$_3$) and sSEBS/silicate, will be prepared using the two approaches in strategy B, respectively. The sSEBS/SrTiO$_3$ nanocomposites will be prepared via in situ synthesis of SrTiO$_3$ in preformed sSEBS films while the sSEBS/silicate nanocomposites will be prepared via solution casting (or co-assembly) of multi-component solutions.

In the preparation of sSEBS/SrTiO$_3$ nanocomposite films the sol-precipitation method will be selected for the in situ synthesis of SrTiO$_3$ nanoparticles. SrTiO$_3$ precursor molecules will permeate preformed sSEBS films in which SrTiO$_3$ particles will form in domain targeted fashion. It is believed that this is the first reported in situ synthesis of crystalline SrTiO$_3$ in a polymer film combining the sol-precipitation method with the use of a block copolymer template. The dielectric properties of these nanocomposite films will be studied.

The preparation of sSEBS/silicate nanocomposite membranes will follow the similar route reported before by our research group. However, these studies differ from those previous in that sSEBS with high sulfonation degrees were used and there were higher TEOS loadings. The properties of this membrane were studied in the context of direct methanol fuel cell (DMFC) membranes.

Macromolecular Dynamics Investigated by Broadband Dielectric Spectroscopy

Macromolecular or polymer dynamics is of fundamental importance in polymer physics.$^{119,120}$ Since many macroscopic properties of polymers, such as mechanical and thermal, are the reflection of microscopic polymer chain motions, it is important to study polymer dynamics. Viscoelastic phenomena in polymers, including the glass transition,
have been widely studied with dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Modern dielectric spectroscopy is superior to these methods in the sense that the sinusoidal electric field perturbation can be applied over a wide frequency range from $10^{-6}$ Hz to $10^{12}$ Hz over a wide temperature range. By probing the dielectric response of materials, broadband dielectric spectroscopy (BDS) provides an ideal technique to investigate macromolecular dynamics, as well as charge transport and dielectric properties of materials, whose signatures are all on the same spectrum.

In a typical measurement, complex dielectric permittivities ($\varepsilon^*$) are collected over a range of frequency ($f$) for an electrical signal at each given temperature. This signal is weak so as not to perturb the structure or dynamics of the polymer. Interactions between the applied electric field and dipoles in the material allow for the observance of dielectric relaxations (molecular motions). Understanding the interaction mechanism is critical for the analysis of dielectric spectroscopy. When a dielectric material is placed inside an alternating electrical field, polarization will occur depending on the material structure. Major types of polarization in various materials include electronic polarization, ionic (atomic) polarization, orientation polarization, and space charge (interfacial) polarization. Electronic polarization arises because the center of the electron cloud around a nucleus is displaced under an applied electric field. Ionic polarization occurs in ionic materials because cations and anions are displaced in opposite direction each other under an applied field. Orientation polarization can occur in materials composed of molecules that have permanent electric dipole moments. This has been described in the classical theory of Debye. Alignment or orientation of dipoles will occur under an
applied field. Interfacial polarization results from the accumulation of charge at structural interfaces in heterogeneous materials in which two adjacent phases have different conductivities and dielectric permittivities. The total polarization, P, is the sum of all the contributions from the different types of polarization. P is essentially the dipole moment per unit volume. Dielectric constant $\varepsilon$, a reflection of P, depends on the ease with which each type of polarization can occur within the time of each reversal of the applied field. The dielectric permittivity as measured in an alternating field consists of a real part and an imaginary part. The real part, $\varepsilon'$, accounts for electrical energy storage and the imaginary part, $\varepsilon''$, accounts for the energy loss per cycle of alternating applied electric field. The dissipation factor, similar to that in dynamic mechanical analysis, is $\tan \delta = \varepsilon''/\varepsilon'$, in which $\delta$ is the phase angle between applied voltage and resulting current.

The time required for polarization reversal is called the relaxation time ($\tau$), and it is related to relaxation frequency (f) by $\tau = 1/(2\pi f_{\text{max}})$. Note that this is a broad electromagnetic spectrum and data in the infrared and visible regions are within the broadband frequency range.

A particular polarization mechanism will not contribute to the total polarization when the half period = $2/f$ of the applied field is much less than the relaxation time, $\tau$. The frequency dependence of the total polarization is illustrated in Figure I-5a. P may lag behind the applied field due to the internal friction - whose source is intermolecular interactions - which leads to energy loss in the material. For each relaxation of polarization the maximum energy loss will occur when the frequency of the applied field is equal to the frequency of associated molecular motions. This characteristic relaxation
frequency corresponds to the peak frequency, $f_{\text{max}}$ in a dielectric loss ($\varepsilon''$) vs. frequency spectrum (Figure I-5b).

**Figure I-5.** Frequency dependence of (a) total polarizability and (b) power loss.$^{124}$

In polymer materials, the observable polarization results mainly from the orientation or alignment of dipoles on polymer molecules. The polarization is essentially the dipole density of $N$ permanent orientable molecular dipoles. However, polymer materials are more complex than low molecular weight compounds with regard to dielectric activity because of wide molecular weight distribution, a huge number of conformations, various architectures of polymer chains, different morphology, glassy vs. rubbery vs. melt states, amorphous to semicrystalline, and a variety of interactions
between polymer chains. All these factors will affect the orientation processes of dipoles. Generally, macromolecular motions are controlled by different time and length scales, resulting in multiple relaxation behavior where each process is indicated by a peak in $\varepsilon''$ and a step-like decrease in $\varepsilon'$ versus frequency at a fixed temperature. In analyzing dielectric spectra the relaxation times ($\tau$) corresponding to each type of molecular motions are extracted from model functions. Since polymers do not show pure Debye, but modified Debye behavior, the Cole/Cole, Cole/Davidson and Havriliak/Negami functions are usually employed. In addressing polymer systems, the phenomenological Havriliak/Negami (HN) equation (Eq. 4) shows strong adaptability to polymers and complex systems, and is given below.

$$
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = -i \left( \frac{\sigma_0}{\varepsilon_0 \omega} \right)^N + \sum_k \left[ \frac{\Delta\varepsilon_k}{1 + (i \omega \tau_{HN})^\alpha} + \varepsilon_\infty \right] 
$$  \hspace{1cm} \text{Eq. 4}

$\varepsilon^*$ is the complex permittivity for which $\varepsilon'$ and $\varepsilon''$ are the real and imaginary parts, respectively. $\omega = 2\pi f$. $k$ is the number of relaxation peak curves used in the curve fitting process. $\Delta\varepsilon_k = (\varepsilon_s - \varepsilon_\infty)_k$ is the relaxation strength for relaxation $k$ where $\varepsilon_s$ and $\varepsilon_\infty$ are the real permittivities at limiting low and high frequency, respectively. $\tau_{HN}$ is the Havriliak-Negami relaxation time. $\alpha$ and $\beta$ are parameters that quantify the breadth and asymmetry, respectively, of a given relaxation peak. $\sigma_0$ is the dc conductivity due to either inherent charge carriers or impurities. The exponent $N$ characterizes the nature of the charge hopping process. The actual relaxation time, or characteristic time scale over which molecular motions occur, is $\tau_{max} = 1/(2\pi f_{max})$, where $f_{max}$ is the frequency at the maximum in $\varepsilon''$, is calculated using the equation:
\[ \tau_{\text{max}} = \tau_{\text{HN}} \left[ \frac{\sin \left( \frac{\pi \alpha \beta}{2(\beta + 1)} \right)}{\sin \left( \frac{\pi \alpha}{2(\beta + 1)} \right)} \right]^{1/\alpha} \]  

Eq. 5

There are as many terms in the sum in equation 1 as there are observed relaxations. Relaxation information was extracted by fitting the Havriliak-Negami (HN) equation, containing a correction for dc conductivity, to experimental imaginary dielectric permittivity \( \varepsilon'' \) data.

BDS has been applied to the study of many polymer systems, including amorphous\textsuperscript{128}, semicrystalline\textsuperscript{129} and block copolymers,\textsuperscript{130} as well as polymer liquid crystals,\textsuperscript{131} blends,\textsuperscript{132} solutions and polymer composites.\textsuperscript{133,134,135} In this research, the macromolecular dynamics of a block copolymer will be studied.

**Summary**

In situ synthesis of inorganic nanoparticles in polymer solutions or polymer film templates affords opportunities in controlling of particle size and dispersion in polymer matrices by adjusting interactions between inorganic and organic inclusions, and development of novel functional materials for wide applications.

In this research, sSEBS/SrTiO\textsubscript{3} and sSEBS/silicate nanocomposite films were prepared and studied, including the macromolecular dynamics. In the study of sSEBS/SrTiO\textsubscript{3}, crystalline SrTiO\textsubscript{3} nanoparticles were formed in the functionalized SEBS template and the effect of this template on the evolution of nanoparticles is discussed. The dielectric enhancement was achieved with the introduction of SrTiO\textsubscript{3} nanoparticles.

In the study of sSEBS/silicate membranes, the effect of sSEBS sulfonation degree and silicate uptake on morphology of nanocomposite membranes is discussed. The morphology and methanol permeability, proton conductivity relationships will provide
guidance for future design and development of polymer nanocomposite membranes as fuel cell polymer electrolyte membranes.

Complemented by DMA results, the relaxation times of block segmental motions in sulfonated SEBS were quantified by BDS. The direct current (dc) conductivity and relaxation time of segmental chain motion was also correlated and the results give insight into the use of sulfonated block copolymers in the area of proton exchange membranes for fuel cells in the sense of understanding the coupling of chain dynamics with charge transport.
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CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLY[(STYRENE-B-(ETHYLENE-CO-BUTYLENE)-B-STYRENE)/STRONTIUM TITANATE NANOCOMPOSITES

Abstract

Polymer-inorganic nanocomposite films were prepared via in situ syntheses of strontium titanate (SrTiO$_3$) nanoparticles in preformed films of sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene] (sSEBS) block copolymers. During the preparation, the SrTiO$_3$ precursors were permeated selectively into target domains in the block polymer film template which was intended to control the subsequent formation and growth of crystalline nanoparticles through hydrolysis and precipitation reactions. FTIR spectra verified the composition of SrTiO$_3$ and X-ray diffraction patterns identified crystalline SrTiO$_3$ within the block copolymer templates. Tapping-mode AFM phase images for both unfilled sSEBS and sSEBS/SrTiO$_3$ films showed nanophase separation characterized by lamellar morphologies which indicated that introduction of SrTiO$_3$ particles did not alter the morphology of the block polymer template. Uniform dispersion of Ti and Sr elements along the nanocomposite film thickness was verified using ESEM/EDX on cross-sections. In TEM images of sSEBS/SrTiO$_3$, clusters of SrTiO$_3$ consisted of parallel rods were found to selectively grow in sulfonated styrene domains in sSEBS film. The very good agreement of the width of SrTiO$_3$ rods in TEM images with the domain size in AFM images confirms the polymer template has strong control over the formation and growth of SrTiO$_3$ inclusion. Selected area electron diffraction of targeted SrTiO$_3$ clusters inside sSEBS/SrTiO$_3$ provided direct identification of in situ
formation of crystalline SrTiO$_3$ particles. Dielectric measurement exhibited increase of
dielectric constant and shifting of dielectric dissipation factor to higher frequency
resulting from introduction of SrTiO$_3$ particles. This increase in dielectric permittivity
affords this type of nanocomposites potential application for energy storage and
conversion devices.

Introduction

Polymer-inorganic nanocomposites as extreme dielectric materials have received
considerable attention for potential applications in electrical energy storage,\textsuperscript{1,2,3,4} thin-film
transistors,\textsuperscript{5} embedded capacitors,\textsuperscript{6,7} and high K gate dielectrics.\textsuperscript{8} Conventional ceramic
materials, such as strontium titanate (SrTiO$_3$) or barium titanate (BaTiO$_3$), have high
dielectric constants on the order of hundreds or even thousands, but they have low
dielectric strength.\textsuperscript{9,10} Dielectric strength is important for energy storage materials. The
energy density of a dielectric capacitor can increase with dielectric strength. The energy
stored by a capacitor is given by $W = (CV_{bd}^2)/2$, where $C$ is the capacitance and $V_{bd}$ is the
breakdown voltage. This is the maximum energy that can be stored before the dielectric
fails at high field strength. In terms of the dielectric constant ($\varepsilon_r$), the volumetric energy
density of a dielectric capacitor is $\tilde{W} = W/(Ad) = (\varepsilon_0\varepsilon_rE_{bd}^2)/2$, where $A$ is area of
dielectric film, $d$ is the thickness of dielectric film, and $\varepsilon_0$ is permittivity of vacuum, $\varepsilon_r$ is
relative permittivity, and $E_{bd} = V_{bd}/d$ is the breakdown field strength (dielectric
strength).\textsuperscript{11} Polymers usually show low dielectric constant, but high dielectric strength.
Polymer nanocomposites formed by combining such ceramic powders with high
dielectric constants and polymers with high dielectric strength have great potential so that
dielectric permittivity can be tailored to be high and the materials are flexible, which may be another beneficial property.\textsuperscript{12}

Currently, the major strategy for preparation of polymer composites as extreme dielectrics is by blending of such ceramic particles in polymer melts or solutions.\textsuperscript{13,14} This simple physical mixing of ceramic particles in a polymer host generally results in poor film quality and inhomogeneity that are mainly caused by agglomeration of ceramic particles. Controlled particle dispersion is extremely important. One approach to prevent particle agglomeration involves addition of surfactant.\textsuperscript{15} However, residual free surfactant can lead to high leakage current and dielectric loss.\textsuperscript{16} Another approach is direct surface treatment of ceramic particles via chemically bonding of organic moieties to enhance dispersibility.\textsuperscript{17,18}

One alternate approach, the in situ synthesis of particles within a polymer template environment, has been studied for preparation of polymer nanocomposites.\textsuperscript{19,20} In this method, a preformed polymer film is immersed in a solution of inorganic particle precursor molecules that diffuse into the polymer film template wherein in situ sol-gel reactions occur in targeted regions.\textsuperscript{21} Using this method, Mauritz et al. prepared various polymer nanocomposites containing different inorganic phases such as SiO\textsubscript{2}, TiO\textsubscript{2} and ZrO\textsubscript{2}\textsuperscript{22,23,24,25} Specifically, when block copolymer films was used, the inorganic particles were shown to selectively initiate and grow in hydrophilic domains due to the chemical affinity between functional groups in polymer and in the precursors molecules.\textsuperscript{26} One advantage of this approach is the good control of particles size and distribution attributed to the template effect of block copolymer films.
Conventional preparation of crystalline MTiO$_3$ (M = Ba or Sr) usually proceeds by calcination of MO or MCO$_3$ (M = Ba or Sr) and TiO$_2$ at very high temperatures, generally > 1000 °C, in order to facilitate the diffusion of metal cations so that they can combine into crystal structures.$^{27,28}$ To realize in situ synthesis of crystalline MCO$_3$ (M = Ba or Sr) within polymer templates which degrade at much lower temperatures, a suitable method for low-temperature formation of crystalline MTiO$_3$ particles is required. In recent years, some methods for low-temperature preparation of crystalline MTiO$_3$ have been reported, including the sol-gel method,$^{29,30,31}$ hydrothermal method,$^{32,33}$ and sol-precipitation method (or alkoxide-hydroxide route),$^{34,35}$ in which MTiO$_3$ nanoparticles are prepared in a liquid phase at low temperature (≤ 100 °C).

The first step in the preparation of MTiO$_3$ crystals using the sol-precipitation process consists of causing hydrolysis and condensation reactions of Ti(OR)$_4$ which results in the formation of a gel of hydrated titanium oxide that has numerous uncondensed TiOH groups. Then, an aqueous M(OH)$_2$ solution is added to the TiO$_2$ gel products where M$^{2+}$ cations permeate into the gel, leading to the formation of crystalline MTiO$_3$ with precipitation. In a more widely used way, barium or strontium salts, such as BaCl$_2$ or Sr(NO$_3$)$_2$, respectively, and a strong base, such as NaOH or KOH (instead of using the metal hydroxide M[OH]$_2$) are added to the reaction system of Ti(OR)$_4$ hydrolysis products in sequence.$^{36,37}$ The widely accepted two-step process mechanism for sol-precipitation is summarized in the following equations.$^{38,39,40}$

\[
\begin{align*}
    Ti(OR)_4 + 2H_2O & \rightarrow TiO_2 (gel) + 4ROH & \text{Eq. 1} \\
    TiO_2 (gel) + M(OH)_2 & \rightarrow MTiO_3 + H_2O & \text{Eq. 2}
\end{align*}
\]
In the synthesis of SrTiO$_3$ with this method, factors that influence the evolution of crystalline particles include: stir speed, temperature, pH, reactant concentration, reactivity of reactants and reactivity of the TiO$_2$ gel.$^{40}$ A strong alkaline environment is critical for the formation of crystalline structures.$^{38}$ The absorption rate of Sr(OH)$_2$ is closely related to the morphology of the SrTiO$_3$ particles.$^{40}$ Low absorption rates tend to yield uniform SrTiO$_3$ particles.

The preparation of polymer/MTiO$_3$ (M = Ba or Sr) nanocomposites via in situ synthesis is challenging because of the difficulty in synthesizing crystalline MTiO$_3$ in a polymer template.$^{41}$ In the study of Lee et al., hydroxylated poly(styrene-b-butadiene-b-styrene) thin films (thickness < 50 nm) were used as template that allowed barium titanium double alkoxide (BaTi[OCH$_2$CH(CH$_3$)OCH$_3$]$_6$) to diffuse into them in solution for 1 hour.$^{42}$ The alkoxide-thin films prepared above were placed in three bottles respectively under three different ways: (1) immersed in H$_2$O, (2) immersed in 1 M NH$_4$OH(aq), and (3) placed in an NH$_3$/H$_2$O atmosphere. Then all these three bottles were capped and stored in oven at 80°C for 24 hours. Only in the third way was crystalline BaTiO$_3$ was formed, while amorphous BaTiO$_3$ particles were formed in the other two ways. In another synthesis effort involving polymer/BaTiO$_3$ nanocomposites synthesized from BaTiO$_3$ precursors, a polymer/precursor film was cast from a solution of poly(styrene-co-maleic anhydride) and titanium diisopropoxide bis(ethylacetoacetate) (TIBE). This was followed by reaction in an aqueous solution of Ba(OH)$_2$. Crystalline BaTiO$_3$ particles were identified and dispersed preferentially in spherical maleic-anhydride (MAH) block domains due to the interaction between TIBE precursors and
MAH blocks. However, a continuous layer of BaTiO$_3$ was also formed on the film surface, which is undesirable.

In this work, we report a novel method for the synthesis of crystalline SrTiO$_3$ particles in a phase separated block copolymer film template. The prepared sSEBS/SrTiO$_3$ films were characterized by various techniques. X-ray diffraction (XRD) characterization identified the crystalline structure of SrTiO$_3$ in sSEBS films. The crystalline identity was further proved by TEM/SAED patterns focused on nanocomposite film cross sections. AFM images showed that the natural block copolymer lamellar morphology persisted after the insertion of SrTiO$_3$ nanoparticles in this way. TEM micrographs exhibited well defined clusters of SrTiO$_3$ nanoparticles which were dispersed along the hydrophilic domains. The enhancement of dielectric permittivity at high frequency range was also demonstrated using broadband dielectric spectroscopy. To the best of our knowledge, is the first report of preparation of sSEBS/SrTiO$_3$ nanocomposites via in situ synthesis of crystalline SrTiO$_3$ in a block copolymer template.

**Experimental**

**Materials**

All reagents were used without further purification. The SEBS tri-block copolymer, commercial Kraton® of G1652M grade, was obtained from Kraton® LLC. $M_n$ was ~48,000 g/mol, the polydispersity index was ~1.04 (by GPC), and the styrene block content was ~30 wt% as determined from $^1$H NMR. Toluene, isopropanol (Pr$_3$OH), 1,2-dichloroethane (DCE) (99.8%), acetic anhydride (ACS grade), and sulfuric acid (ACS grade) were obtained from Fisher Co. Acetylacetone (99%), titanium (IV) isopropoxide
[Ti(OPr)i]4, 98% and strontium nitrate [Sr(NO3)2, 99%] were obtained from Acros Organics.

**Sulfonation of SEBS.** SEBS was sulfonated according to the procedure earlier reported by Mauritz et al.43 SEBS was dissolved in DCE at 50 °C. The sulfonating agent, acetyl sulfate, was generated by addition of sulfuric acid to a solution of acetic anhydride in DCE. The amount of acetyl sulfate required for the desired level of sulfonation was added to the polymer solution. The reaction proceeded for ~3-4 h and the polymer was recovered by steam stripping. The sSEBS sample was then dried under vacuum at 50 °C for longer than 5 d until constant mass was achieved. The sulfonation level of sSEBS was determined by titration. The sulfonated samples were dissolved in a toluene/hexanol (85/15 volume ratio) mixture with a concentration of 0.2~0.4% g/mL. This solution was titrated against 0.05M NaOH standard solution in methanol to a phenolphthalein endpoint. The normality of the standard solution was determined by 0.01 M p-toluene sulfonic acid in methanol. The degree of sulfonation (x%) is the molar percentage of styrene repeat units sulfonated; each sulfonated sample is denoted as sSEBS(x%).

**Preparation of sSEBS/SrTiO3 membranes via in situ synthesis of SrTiO3 in preformed sSEBS films.** The preformed sSEBS films were prepared by casting solutions of sSEBS in toluene/isobutanol co-solvent into Teflon dishes, followed by their drying at 50 °C in an oven for 5 days and annealing at 120 °C in vacuum oven for 2 days. All sSEBS film samples have thicknesses in the range 0.1-0.2 mm. In a typical preparation of sSEBS/SrTiO3 films, sSEBS films preformed in this way were punched into disc samples with diameter of 22 mm and immersed in isopropanol for more than two days to allow sufficient swelling. A clear yellow solution of complex of Ti(OPr)i4 and acetylacetone
was prepared by addition of 6 mL Ti(OPr)i₄ into 8.15 mL acetylacetone (molar ratio = ¼) in three-neck 100 mL flask under stir at room temperature and diluted by addition of isopropanol. The swollen sSEBS films were transferred to this newly prepared solution of Ti(OPr)i₄ complexes to allow the permeation of the titanium complex into sSEBS films while stirring at room temperature over 10 h. After removing the sSEBS film samples, 5.66 mL DI H₂O was dropped into the above solution under stirring and the solution remained transparent. The sSEBS film samples were returned to the hydrolyzed solution to allow further permeation for 2 h, followed by addition of 15 mL of 1.31M Sr(NO₃)₂ aqueous solutions while keeping the molar ratio of strontium to titanium at 1. Then, 50 mL of 5M NaOH aqueous solution was slowly added into above hydrolyzed solution. The reaction system was heated in an oil bath at 90 °C, under stirring, for over 15 hours, and then cooled to room temperature naturally. The in situ formation of SrTiO₃ in sSEBS resulted in sSEBS/SrTiO₃ nanocomposite films, while white SrTiO₃ particles dispersions were formed in the liquid phase. The SrTiO₃ particles formed in the reaction solution were collected by repeated procedures including solution neutralization with hydrogen chloride, centrifugation and re-dispersion of white SrTiO₃ particles in DI water until the pH value showed ~7 with pH paper. The white powder of SrTiO₃ was obtained by drying the wet particles in a drying oven at 80 °C under vacuum for 24 h. sSEBS disc samples were washed with isopropanol and DI water repeatedly to remove excess SrTiO₃ attached to film surfaces and impurities inside the film. Final film samples were obtained by drying in an oven at 100 °C under vacuum for 24 h. The SrTiO₃ content in sSEBS/SrTiO₃ were determined by TGA. Each nanocomposite sample is noted as
sSEBS(x%)/SrTiO$_3$(y%), where x% represents the sulfonation degree of the sSEBS matrix and y% represents weight percent of inorganic inclusions.

**Film Characterization**

*FTIR spectroscopy.* FTIR spectra were acquired in attenuated total reflectance (ATR) mode using a Bruker Equinox 55 spectrometer with 128 scans at a resolution of 4 cm$^{-1}$.

*X-ray diffraction (XRD).* The structure and size of SrTiO$_3$ crystals in powders and in sSEBS/SrTiO$_3$ films were characterized using a Rigaku Ultima III X-ray diffractometer using Cu K$\alpha$ radiation of wavelength 1.54 Å. X-ray scans were performed in the 2$\theta$ angle range of 10 to 90°. The d spacing and crystallite size of samples was calculated from diffraction patterns using software MDI Jade 6.0.

*Atomic force microscopy (AFM).* Tapping mode atomic force microscopy (TM-AFM) phase images were obtained using a Digital Instruments Dimension 3000 scanning probe microscope at ambient conditions. Samples for AFM analysis were sectioned with a diamond knife at -75 °C using a Leica EM UC6 Ultra Cryo-microtome system in order to create a flat surface for observation. All film samples were embedded in thermosetting epoxy resin capsules to provide sufficient support in the microtome process.

*Environmental scanning electron microscopy/energy dispersive X-ray spectroscopy (ESEM/EDX).* The local elemental composition on the film surface and cross-sections of sSEBS/SrTiO$_3$ films was investigated by the use of energy dispersive X-ray analysis spectroscopy (EDX) using an FEI Quanta 200 SEM equipped with a NORAN System 7 X-ray microanalysis system. Energy dispersive spectra were measured using an accelerating voltage of 20 kV under two different modes: Point & Shoot mode.
and Linescan mode. The specimens were prepared by fracturing them in liquid nitrogen and were used for observation without gold sputtering. The analysis method consistently provides elemental detection limits of approximately 1000 parts per million (or 0.1 wt %) and provides for the identification and quantification of individual elements present at different points in a sample.

*Transmission electron microscope (TEM).* Morphological images of sSEBS/SrTiO$_3$ samples were obtained using a JEOL JEM-2100 Transmission Electron Microscope (TEM) equipped with an energy dispersive X-ray microanalysis (EDX) detector at 200 kV. The sections of samples with thickness of 100 nm were cut by using a diamond knife at -75 °C with Leica EM UC6 Ultra Cryo-microtome system, and collected using 200 mesh carbon-coated copper grids. All film samples were embedded in epoxy resin capsules to provide sufficient support in microtoming. For TEM/EDX analysis, electron beams were irradiated onto target areas in Linescan mode, and the emitted X-rays were analyzed with specific EDX spectra counts for 10 s. Selected area electron diffraction (SAED) patterns for target areas were obtained to identify crystalline structures of typical particles inserted inside the sSEBS matrix.

*Broadband dielectric spectroscopy (BDS).* Isothermal dielectric spectra were collected using a Novocontrol GmbH Concept 80 Broadband Dielectric Spectrometer over the frequency ($f$) range of 0.01 Hz - 3 MHz and over the temperature range of -110 to 220 °C. Temperature stability was controlled to within ±0.2 °C. Disc samples of sSEBS/SrTiO$_3$ membranes with diameter of ~2 cm were covered with two thin aluminum sheets on both sides and then sandwiched between two gold-coated copper electrodes of 2 cm diameter and transferred to the instrument chamber for measurement.
Results and Discussion

Preparation of sSEBS/SrTiO<sub>3</sub> Films

The process of synthesizing sSEBS/SrTiO<sub>3</sub> nanocomposites is illustrated in Figure II-1. The formation of SrTiO<sub>3</sub> inside a sulfonated SEBS film consisted of the following steps: (1) formation of Ti(OPr<sup>i</sup>)<sub>4-x</sub>(acac)<sub>x</sub> complexes, (2) permeation of Ti(OPr<sup>i</sup>)<sub>4-x</sub>(acac)<sub>x</sub> into swollen sSEBS films, (3) formation of swollen, amorphous TiO<sub>2</sub> gel particles (having TiOH groups throughout) through the hydrolysis of Ti(OPr<sup>i</sup>)<sub>4</sub>-x(acac)<sub>x</sub>, (4) diffusion of Sr<sup>2+</sup> into the TiO<sub>2</sub> gel particles, (5) nucleation of SrTiO<sub>3</sub> and (6) growth of crystalline SrTiO<sub>3</sub> particles. During the preparation of nanocomposite films, white SrTiO<sub>3</sub> particles were also synthesized in the reaction solution during this time.

Equation 3 shows the titanium complex formation reaction.

\[ Ti(\text{OPr}^{i})_4 + x (\text{acacH}) \rightarrow Ti(\text{OPr}^{i})_{4-x}(\text{acac})_x + x Pr^{i}OH \quad \text{Eq. 3} \]
NaOH aqueous solution in excess was added during the reactions to neutralize the \( \text{SO}_3\text{H} \) groups and provide an alkaline environment. But excessive NaOH may not be good, because \( \text{Sr(OH)}_2 \) solubility in water may decrease by very high concentration of NaOH in solution, so that the \( \text{Sr}^{2+} \) concentration goes down.

Representative ATR-FTIR spectra of sSEBS and sSEBS/SrTiO\(_3\) samples are displayed in Figure II-2. The difference between the spectra of sSEBS and sSEBS/SrTiO\(_3\) mainly arise from the introduction of bands characteristic of SrTiO\(_3\). In sSEBS/SrTiO\(_3\) samples, the replacement of \(-\text{SO}_3\text{H}\) with \(-\text{SO}_3\text{M}\) (M = \(\text{Sr}^{2+}, \text{Na}^+\)) affects the peaks associated with this group. In the spectrum of sSEBS(38.1%), the absorption at 1124 cm\(^{-1}\) is attributed to symmetric S-O stretching vibration in the \(-\text{SO}_3^-\) group, while the absorption at 1001 cm\(^{-1}\) is due to the in-plane bending vibration of a di-substituted benzene ring with the substitution of one \(-\text{SO}_3^\text{-}\) group.\(^{46}\) The peaks at 1367 cm\(^{-1}\) and 1157 cm\(^{-1}\) are due to asymmetric and symmetric stretching of the \(\text{O}=\text{S}=\text{O}\) groups in \(-\text{SO}_3\text{H}\) groups, respectively. The peaks at 1205 cm\(^{-1}\) and 1034 cm\(^{-1}\) are assigned to asymmetric and symmetric stretching vibration of S-O bond of the \(-\text{SO}_3\text{H}\) respectively.\(^{47}\) In comparison to pure sSEBS, the major change in the sSEBS matrix after the formation of SrTiO\(_3\) particles is the exchange of hydrogens with metal cations such as \(\text{Ti}^{4+}, \text{Sr}^{2+}, \text{or Na}^+\). In the spectrum of sSEBS(65.0%)/SrTiO\(_3\), the absorbance at \(\sim1182\) cm\(^{-1}\) and 1039 cm\(^{-1}\) are attributed to the asymmetric and symmetric stretching vibration of the S-O bond of the \(-\text{SO}_3^-\) anion respectively. The characteristic peaks at 1124 cm\(^{-1}\) and 1007 cm\(^{-1}\) are due to the in-plane skeletal vibration of benzene rings substituted by \(-\text{SO}_3^-\) and \(-\text{SO}_3\text{M}\) respectively.\(^{49}\) The peak at 698 cm\(^{-1}\) arose from the C-H stretching of the benzene ring.\(^{48}\)
Figure II-2. Infrared spectra of (a) sSEBS(38.1%), (b) sSEBS(65.0%), (c) sSEBS(38.1%)/SrTiO$_3$(13.5%) and (d) sSEBS(65.0%)/SrTiO$_3$(11.1%).

The inorganic uptake in nanocomposite films was calculated by residual char weight percentage in sSEBS/SrTiO$_3$ subtracting char weight percentage in relevant sSEBS, in which weight residual was given by TGA results. The inorganic content in sSEBS(38.1%)/SrTiO$_3$ was 13.5wt%, while the content in sSEBS(65%)/SrTiO$_3$ was 11.1wt%. The inorganic content is determined by the absorption of Ti precursor and Sr$^{2+}$ in sSEBS film during the preparation. Generally, the sSEBS with higher sulfonation degree exhibited stronger ability to absorb inorganic precursors. In a designed comparison, the sSEBS(14.4%) showed only ~2wt% absorption of titanium precursors.
after permeation for 12 hours, while both sSEBS(38.1%) and sSEBS(65.0%) showed absorption more than 15wt%.

Film Characterization

X-ray diffraction (XRD) analysis of crystal structure. All sSEBS/SrTiO$_3$ films and powder samples were characterized using the X-ray diffractometer to identify SrTiO$_3$ crystal structure. The XRD spectrum of SrTiO$_3$ powders (no polymer present) collected from the reaction solution showed well-resolved peaks on a flat baseline, suggesting the formation of crystalline SrTiO$_3$ (Figure II-3). All of the observed XRD peaks were consistent with XRD patterns of cubic SrTiO$_3$ reported in the literature, and they were assigned to corresponding Miller indices.$^{49,50}$ The Bragg spacings ($d_{hkl}$) were calculated from Bragg’s law (Eq.4), and the mean crystallite size ($B$) of SrTiO$_3$ particles were determined by the use of the Scherrer formula (Eq.5) and the results are tabulated in Table II-1.$^{51,52}$

$$n\lambda = 2d_{hkl} \sin \theta$$
Eq. 4

$$B(2\theta) = \frac{0.9\lambda}{L\cos \theta}$$
Eq. 5

$\lambda$ is the wavelength of incident X-radiation (0.154 nm), L is the peak width at half maximum and $\theta$ is one half of the diffraction angle $2\theta$. For all the diffraction peaks applied, the calculated crystallite size is in the range of 20-30 nm.
Figure II-3. Wide angle X-ray diffraction pattern of SrTiO$_3$ powder prepared in the synthesis of sSEBS(38.1%)/SrTiO$_3$(13.5%) nanocomposite film.

Table II-1. Calculated d-spacings, Crystallite Sizes and Miller Indices Based on the X-ray Diffraction Pattern of SrTiO$_3$ Powders Prepared Concurrently with the Synthesis of sSEBS(38.1%)/SrTiO$_3$(13.5%) Nanocomposite Film

<table>
<thead>
<tr>
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<th>d-spacing (Å)</th>
<th>Intensity (%)</th>
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<td>1.24</td>
<td>17.2</td>
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The XRD pattern of sSEBS(38.1%)/SrTiO$_3$(13.5%) film in Figure II-4 exhibited clear diffraction peaks, which is in good agreement with those in the SrTiO$_3$ powders, which suggests the successful in situ formation of crystalline particles inside the polymer
film. The crystallite sizes of SrTiO$_3$ inside composite film determined by the Scherrer formula were in the range of 15-20 nm (Table II-2).

![X-ray diffraction pattern of sSEBS(38.1%)/SrTiO$_3$(13.5%) nanocomposite film](image)

**Figure II-4.** Wide Angle X-ray diffraction pattern of sSEBS(38.1%)/SrTiO$_3$(13.5%) nanocomposite film.

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<th>Crystallite size (Å)</th>
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**Table II-2.** Calculated d-spacings, Crystallite Sizes and Miller Indices Based on the X-ray Diffraction Pattern of an sSEBS(38.1%)/SrTiO$_3$(13.5%) Nanocomposite Film

The XRD spectra of both SrTiO$_3$ powders, collected from the solution in the preparation of sSEBS(65.0%)/SrTiO$_3$(11.1%) and sSEBS(65.0%)/SrTiO$_3$(11.1%) film also exhibit crystalline peaks of SrTiO$_3$ (Figure II-5 and Figure II-6). The mean crystallite sizes of
SrTiO$_3$ powders are in 14-25 nm, while the counterparts in composite films are in 17-24 nm (Table II-3 and Table II-4). In short, these sizes are approximately equal.

![Figure II-5. Wide angle X-ray diffraction pattern of SrTiO$_3$ powder prepared in the synthesis of sSEBS(65.0%)/SrTiO$_3$(11.1%) nanocomposite film.](image)

**Table II-3.** Calculated d-spacings, Crystallite Sizes and Miller Indices Based on the X-ray Diffraction Pattern of SrTiO$_3$ Powder Prepared in Synthesis of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Nanocomposite Film

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Figure II-6. Wide angle X-ray diffraction pattern of sSEBS(65.0%)/SrTiO$_3$(11.1%) nanocomposite film.

Table II-4. Calculated d-spacings, Crystallite Sizes and Miller Indices Based on an X-ray Diffraction Pattern of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Nanocomposite Film

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</table>

An sSEBS(14.4%) film was also used to prepare nanocomposites. However, the XRD pattern of sSEBS(14.4%)/SrTiO$_3$ did not show the crystalline structure of SrTiO$_3$. The sSEBS(14.4%) film showed only ~2 wt% absorption of inorganic precursors which may be an insufficient concentration inside the film to combine the ions in the correct proportions. In fact it has been shown that a sufficient concentration is necessary to form crystalline SrTiO$_3$ in liquid phase.$^{41}$
Atomic force microscopy. Tapping mode AFM/phase images of sSEBS(38.1%) and sSEBS(38.1%)/SrTiO$_3$(13.5%) films are illustrated in Figures II-7a and II-7b. Both images reveal well defined overall lamellar morphology with domain sizes in the range of 20-30 nm. The dark regions are assigned to the hydrophilic sulfonated styrene block domains and the bright regions correspond to the hydrophobic ethylene/butylene block domains. These results, in comparison, indicate that the polymer film template remained almost unchanged after insertion of SrTiO$_3$ phase. In Figure 7b small particles were identified and mainly dispersed in dark regions that are hydrophilic domains. This selective formation of SrTiO$_3$ nanoparticles in hydrophilic domains suggests the desired polymer template effect due to the phase separated morphology and the affinity between the ionic inorganic precursors and hydrophilic blocks.

![Figure II-7. TP-AFM phase images of a) sSEBS(38.1%) film and b) sSEBS(38.1%)/SrTiO$_3$ film; both scan boxes are 2 µm x 2 µm, phase scales are 0-40°, and 0-60°, respectively.](image)

In Figure II-8a, a sSEBS(65.0%) film exhibits a similar lamellar morphology as sSEBS(38.1%). Figure II-8b shows the sSEBS(65.0%)/SrTiO$_3$(11.1%) film remain lamellar morphology after introduction of SrTiO$_3$ particles, suggesting, again, a polymer template effect.
Figure II-8. TP-AFM phase images of a) sSEBS(65.0%) film and b) sSEBS(65.0%)/SrTiO$_3$(11.1%) film; both scan boxes are 2 µm x 2 µm, phase scales are 0-60°, and 0-90° respectively.

*ESEM/EDX.* The elemental compositions of sSEBS/SrTiO$_3$ across film cross sections and the film surfaces were analyzed by EDX. In Figure II-9, carbon (C), oxygen (O), sodium (Na), sulfur (S), titanium (Ti), and strontium (Sr) were identified in the five squares along the sSEBS(38.1%)/SrTiO$_3$(13.5%) film thickness and their weight percentages and atomic percentages were measured and listed in Tables II-5 and II-6. The sulfur composition was attributed to sulfonic acid groups in styrene blocks.

**Table II-5.** Weight Percentage of Elements in Square Regions of an sSEBS(38.1%)/SrTiO$_3$(13.5%) Film Cross-section Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>88.2</td>
<td>5.7</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Square 2</td>
<td>86.3</td>
<td>7.8</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Square 3</td>
<td>90.4</td>
<td>4.0</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Square 4</td>
<td>88.1</td>
<td>5.5</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Square 5</td>
<td>88.6</td>
<td>4.7</td>
<td>1.3</td>
<td>1.2</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Average</td>
<td>88.3</td>
<td>5.5</td>
<td>1.4</td>
<td>1.1</td>
<td>1.0</td>
<td>2.7</td>
</tr>
</tbody>
</table>
The Na, Ti, and Sr elemental compositions are due to the absorption of the inorganic precursors (i.e., NaOH) and subsequent SrTiO$_3$ that formed in situ. Except for oxygen, all other elements showed similar contents in each square, suggesting uniform composition along the film thickness. The atomic percentage sum of Ti, Sr and Na is far more than the percentage of sulfur, indicating strong absorption ability of the sulfonic acid domains. The atomic percentage of Sr showed 50% more than Ti.

**Figure II-9.** (a) SEM micrograph of sSEBS(38.1%)/SrTiO$_3$(13.5%) film cross-section showing five squares that were selected for EDX analysis along the film thickness; (b) an typical EDX spectrum of square 2 of sSEBS(38.1%)/SrTiO$_3$(13.5%) film cross-section.
Figure II-10 shows the ESEM/EDX micrograph and the EDX spectrum at the sSEBS(38.1%)/SrTiO$_3$(13.5%) film surface. In each square, each element shows similar content, suggesting uniform absorption of metal cations (Table II-7 and II-8). In comparison of film surface to film cross-section, the film surface exhibited 200% more contents in Ti and Sr than those at film cross-section.

**Table II-6.** Atomic Percentage of Elements in Square Regions of an sSEBS(38.1%)/SrTiO$_3$(13.5%) Film Cross-section Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>93.6</td>
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<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Square 2</td>
<td>91.9</td>
<td>6.2</td>
<td>0.8</td>
<td>0.4</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Square 3</td>
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<td>0.8</td>
<td>0.5</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Square 4</td>
<td>93.7</td>
<td>4.4</td>
<td>0.7</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Square 5</td>
<td>94.2</td>
<td>3.8</td>
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<td>0.5</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Average</td>
<td>93.7</td>
<td>4.4</td>
<td>0.8</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**Table II-7.** Weight Percentage of Elements in Square Regions of an sSEBS(38.1%)/SrTiO$_3$(13.5%) Film Surface Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
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<td>16.2</td>
<td>1.2</td>
<td>1.0</td>
<td>3.8</td>
<td>8.3</td>
</tr>
<tr>
<td>Square 2</td>
<td>69.8</td>
<td>15.7</td>
<td>1.2</td>
<td>1.0</td>
<td>3.9</td>
<td>8.5</td>
</tr>
<tr>
<td>Square 3</td>
<td>66.8</td>
<td>18.6</td>
<td>1.3</td>
<td>1.0</td>
<td>3.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Average</td>
<td>68.7</td>
<td>16.8</td>
<td>1.3</td>
<td>1.0</td>
<td>3.8</td>
<td>8.5</td>
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</tbody>
</table>

**Table II-8.** Atomic Percentage of Elements in Square Regions of an sSEBS(38.1%)/SrTiO$_3$(13.5%) Film Surface Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>82.1</td>
<td>14.3</td>
<td>0.8</td>
<td>0.4</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Square 2</td>
<td>82.4</td>
<td>14.0</td>
<td>0.8</td>
<td>0.4</td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>Square 3</td>
<td>79.6</td>
<td>16.7</td>
<td>0.8</td>
<td>0.5</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Average</td>
<td>81.3</td>
<td>15.0</td>
<td>0.8</td>
<td>0.4</td>
<td>1.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>
Figure II-10. (a) SEM micrograph of sSEBS(38.1\%)/SrTiO$_3$(13.5\%) film surface showing three squares that were selected for EXD analysis; (b) an typical EDX spectrum of square 2 of sSEBS(38.1\%)/SrTiO$_3$(13.5\%) film surface.

The cross-sections and surfaces for a sSEBS(65.0\%)/SrTiO$_3$(11.1\%) film were also characterized with ESEM/EDX as illustrated in Figures II-11 and II-12. Along the thickness direction, very high Ti and Sr contents were found in the central square, where Na showed the lowest content. The sulfur content in sSEBS(65.0\%)/SrTiO$_3$(11.1\%) film is almost double the counterpart in the sSEBS(38.1\%)/SrTiO$_3$(13.5\%) film, which is reasonable because the former sSEBS has higher sulfonic acid concentration than the latter.
Figure II-11. (a) SEM micrograph of sSEBS(65.0%)/SrTiO$_3$(11.1%) film cross-section showing five squares that were selected for EDX analysis along the film thickness; (b) an typical EDX spectrum of square 2 of sSEBS(65.0%)/SrTiO$_3$(11.1%) film cross-section.

Table II-9. Weight Concentration Percentage of Elements in Square Regions of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Film Cross-section Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
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<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
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</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>81.5</td>
<td>7.3</td>
<td>1.4</td>
<td>4.2</td>
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<td>3.4</td>
</tr>
<tr>
<td>Square 2</td>
<td>82.7</td>
<td>7.3</td>
<td>1.2</td>
<td>3.5</td>
<td>2.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Square 3</td>
<td>72.7</td>
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<td>0.8</td>
<td>4.5</td>
<td>5.2</td>
<td>4.0</td>
</tr>
<tr>
<td>Square 4</td>
<td>85.1</td>
<td>7.2</td>
<td>1.6</td>
<td>2.7</td>
<td>1.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Square 5</td>
<td>81.9</td>
<td>9.0</td>
<td>1.5</td>
<td>2.6</td>
<td>1.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Average</td>
<td>80.8</td>
<td>8.7</td>
<td>1.3</td>
<td>3.5</td>
<td>2.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Figure II-12. (a) SEM micrograph of sSEBS(65.0%)/SrTiO$_3$(11.1%) film surface showing three squares that were selected for EXD analysis; (b) an typical EDX spectrum of square 2 of sSEBS(65.0%)/SrTiO$_3$(11.1%) film surface.

The average Sr content (2.5wt%) in sSEBS(65.0%)/SrTiO$_3$(11.1%)film cross-section is far more than that (1.0wt%) in sSEBS(38.1%)/SrTiO$_3$(13.5%) film cross-section. Unlike the comparison of Ti and Sr content in sSEBS(38.1%)/SrTiO$_3$(13.5%) film cross-section, the Ti content is higher than Sr content in sSEBS(65.0%)/SrTiO$_3$(11.1%) film cross-section. The sSEBS(65.0%)/SrTiO$_3$(11.1%) film surface showed relatively even chemical composition in three squares (Table II-11 and II-12). With regard to the comparison of metal absorption at the film surface and film cross-section, sSEBS(65.0%)/SrTiO$_3$(11.1%) film showed much lower Ti and Sr contents at the film surface than those contents at the film cross-section.
Table II-10. Atomic Percentage of Elements in Square Regions of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Film Cross-section Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
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<td>1.7</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Square 2</td>
<td>90.8</td>
<td>6.0</td>
<td>0.7</td>
<td>1.5</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Square 3</td>
<td>84.3</td>
<td>11.1</td>
<td>0.5</td>
<td>2.0</td>
<td>1.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Square 4</td>
<td>91.5</td>
<td>5.8</td>
<td>0.9</td>
<td>1.1</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Square 5</td>
<td>89.7</td>
<td>7.4</td>
<td>0.9</td>
<td>1.1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Average</td>
<td>89.3</td>
<td>7.3</td>
<td>0.8</td>
<td>1.5</td>
<td>0.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table II-11. Weight Percentage of Elements in Square Regions of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Film Surface Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>81.9</td>
<td>12.1</td>
<td>1.8</td>
<td>2.1</td>
<td>0.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Square 2</td>
<td>81.3</td>
<td>12.1</td>
<td>1.8</td>
<td>2.1</td>
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<td>1.7</td>
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<tr>
<td>Square 3</td>
<td>83.3</td>
<td>11.0</td>
<td>1.9</td>
<td>2.1</td>
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<td>1.1</td>
</tr>
<tr>
<td>Average</td>
<td>82.2</td>
<td>11.8</td>
<td>1.8</td>
<td>2.1</td>
<td>0.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table II-12. Atomic Percentage of Elements in Square Regions of an sSEBS(65.0%)/SrTiO$_3$(11.1%) Film Surface Calculated from EDX Spectra

<table>
<thead>
<tr>
<th>Targeted area</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>S</th>
<th>Ti</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square 1</td>
<td>88.0</td>
<td>9.8</td>
<td>1.0</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Square 2</td>
<td>87.8</td>
<td>9.8</td>
<td>1.0</td>
<td>0.9</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Square 3</td>
<td>89.0</td>
<td>8.8</td>
<td>1.1</td>
<td>0.8</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Average</td>
<td>88.3</td>
<td>9.5</td>
<td>1.0</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

TEM investigations of nanocomposite morphology. In Figure II-13 consists of TEM images of cryo-microtomed cross sections of an sSEBS(38.1%)/SrTiO$_3$(13.5%) film showing SrTiO$_3$ particles throughout. The visual contrast in this sample is provided by the great difference in electron density between that of the inorganic particles and organic polymer matrix. The background polymer morphology is not seen because the sulfonated blocks have not been stained as this would have adversely affected the
particles. Most regions of the specimen are dominated by uniformly dispersed clusters of parallel rods as seen in Figure II-13a. The average rod width is in the range of 20-30 nm, which is in good agreement with the domain size of the sulfonated styrene domains seen in the AFM image in Figure II-8a as well as the particle size calculated using the Scherrer equation. This coincidence suggests that the SrTiO$_3$ crystals grow along the hydrophilic styrene block domains, which again supports the concept of a template effect by the block copolymer.

**Figure II-13.** TEM images of sSEBS(38.1%)/SrTiO$_3$(13.5%) film: (a) representative morphology, (b) overlapped clusters, (c) boundary region between sSEBS and epoxy resin, (d) separate SrTiO$_3$ particles.
As illustrated in Figure II-13b, some regions across the specimen show a dense dispersion of dark clusters. This effect is most likely due to the simple overlap of each rod clusters at different depths perpendicular to the plane of the image. Or, some regions of the cross-section may have somewhat different thicknesses than the nominal 100 nm due to cryo-microtoming. Some large well-separated cubic particles in the size range of 150-250 nm were also found in some regions (Figure II-13c and II-13d). To understand the origin of these large particles, TEM/EDX in linescan mode was conducted in these areas in Figure II-14.

![Figure II-14](image)

**Figure II-14.** TEM micrograph and EDX spectra in linescan mode of sSEBS(38.1%)/SrTiO$_3$(13.5%) specimen, accelerate voltage = 200 kV, Magnification = 10000, length of scan line (the black arrow line) = 14 µm.

The significant reduction of sulfur composition to zero over the region suggests that it is the interface between film cross-section and epoxy phase, since the
nanocomposite was embedded in an epoxy capsule before undergoing microtoming. Therefore, it is reasonable to conclude that these large particles, formed in the reactive solution during preparation, were simply attached to the film surface and are not a part of the internal morphology. The appearance of such large particles of different size may be due to Ostwald ripening, which is a well-known phenomenon in the growth of inorganic particles, in which smaller particles are essentially consumed by larger particles during the growth process.\(^\text{53}\)

Figure II-15. TEM/SAED of sSEBS(38.1%)/SrTiO\(_3\)(13.5%) film: (a) Magnified SrTiO\(_3\) cluster (b) the cluster’s SAED pattern, (c) magnified large SrTiO\(_3\) particle on film surface, (d) the large particle’s SAED pattern.

Figure II-15b shows the selected area electron diffraction (SAED) pattern for a beam focused on an SrTiO\(_3\) cluster seen in Figure II-15a inside an
There are faint narrow arcs that indicate crystallinity. The SAED diffraction pattern for the large SrTiO$_3$ particle on the film surface in Figure II-15c is seen in Figure II-15d. The pattern consists of rather discrete organized spots attesting to the crystalline nature of the particle. Further similar studies would include determining the nature of the unit cell.

Figure II-16. TEM/SAED of sSEBS(65.0%)/SrTiO$_3$(11.1%) film: (a) representative morphology, (b) Magnified SrTiO$_3$ cluster, (c) the cluster’s SAED pattern, (d) SAED pattern of a large SrTiO$_3$ particle on film surface.

Figure II-16 shows SAED patterns corresponding to the accompanying TEM images for sSEBS(65.0%)/SrTiO$_3$(11.1%). Figure 16a is a representative morphology for
the cross-section in which SrTiO$_3$ clusters were uniformly inserted in hydrophilic domains. Figure II-16b is a magnified SrTiO$_3$ rod cluster. The electron diffraction pattern for SrTiO$_3$ cluster consists of sharp points rather than rings which suggests a sharp crystalline structure. Figure II-16d is an electron diffraction pattern of a large SrTiO$_3$ particle, which came from attachment to the film surface, and symmetric spot pattern suggested single crystalline structure.

*Dielectric properties of nanocomposites.* Introduction of SrTiO$_3$ nanoparticles was expected to enhance the dielectric properties of the block copolymer template material because of their high dielectric permittivity. Furthermore, the dielectric properties of polymer composites may be influenced by the state of filler dispersion and interfacial polarization at organic/inorganic phase interfaces owing to differences in the real dielectric permittivity between the two phases. The dielectric permittivity for these samples was measured using BDS at room temperature (20 °C). The dielectric frequency dependency of SrTiO$_3$ powders is illustrated in Figure II-17.

**Table II-13.** Dielectric Properties of SrTiO$_3$ Powders Collected from Reaction Solution in Preparation of sSEBS(38.1%)/SrTiO$_3$(11.1%) Film

<table>
<thead>
<tr>
<th>Dielectric</th>
<th>100 Hz</th>
<th>10 kHz</th>
<th>1000 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon'$</td>
<td>15100</td>
<td>5430</td>
<td>1180</td>
</tr>
<tr>
<td>$\varepsilon''$</td>
<td>7060</td>
<td>4040</td>
<td>269</td>
</tr>
<tr>
<td>Tanδ</td>
<td>0.466</td>
<td>0.744</td>
<td>0.227</td>
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</table>

Both storage permittivity ($\varepsilon'$) and dielectric loss ($\varepsilon''$) curve show increase from high to low frequency and one plateau section during middle frequency. $\varepsilon'$ is a measure of the degree to which a material can be polarized at a given frequency at a given temperature. With regard to possible polarization mechanism in SrTiO$_3$ powders, it will undergo spontaneous polarization of crystalline SrTiO$_3$ and interfacial polarization from
high to low frequency. The $\tan\delta$ curve shows two peaks at 2 Hz and 20 kHz. The dielectric values of SrTiO$_3$ powders at given frequency are listed in Table II-13.

**Figure II-17.** Frequency dependence of $\varepsilon'$, $\varepsilon''$, and $\tan\delta$ for SrTiO$_3$ powders collected from reaction solution in preparation of sSEBS(38.1%)/SrTiO$_3$(11.1%) film.

**Figure II-18.** Frequency dependence of dielectric storage ($\varepsilon'$) of sSEBS(38.1%), sSEBS(65.0%), sSEBS(38.1%)/SrTiO$_3$(13.5%), and sSEBS(65.0%)/SrTiO$_3$(11.1%) films at 20 °C.
The frequency dependence of the storage permittivity \( \varepsilon' \) of sSEBS and sSEBS/SrTiO\(_3\) samples for two sulfonation degrees is illustrated in Figure II-18. Figure II-18 shows that SrTiO\(_3\) particle insertion indeed influences the real dielectric permittivity. The sSEBS(65.0%) sample show higher \( \varepsilon' \) than the sSEBS(38.1%) sample over the entire frequency range, owing to the higher concentration of polar SO\(_3\)H groups. The sSEBS(38.1%)/SrTiO\(_3\)(13.5%) sample has higher \( \varepsilon' \) than the unfilled control over most of the high frequency range due to introduction of SrTiO\(_3\) nanoparticles. The sSEBS(65.0%)/SrTiO\(_3\)(11.1%) sample shows higher \( \varepsilon' \) in high frequency range from 1 kHz to 3 MHz. The comparison \( \varepsilon' \) of samples at given frequencies are listed in Table II-14.

**Table II-14.** Dielectric \( \varepsilon' \) of sSEBS and sSEBS/SrTiO\(_3\) at Various Frequencies at 20 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>100 Hz</th>
<th>10 kHz</th>
<th>1000 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS(38.1%)</td>
<td>29.8</td>
<td>6.4</td>
<td>3.4</td>
</tr>
<tr>
<td>sSEBS(65.0%)</td>
<td>3320.0</td>
<td>134.0</td>
<td>6.2</td>
</tr>
<tr>
<td>sSEBS(38.1%)/SrTiO(_3)(13.5%)</td>
<td>202.0</td>
<td>85.4</td>
<td>9.5</td>
</tr>
<tr>
<td>sSEBS(65.0%)/SrTiO(_3)(11.1%)</td>
<td>3210.0</td>
<td>730.0</td>
<td>23.2</td>
</tr>
</tbody>
</table>

**Table II-15.** Dielectric \( \varepsilon'' \) of sSEBS and sSEBS/SrTiO\(_3\) at Various Frequencies at 20 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>100 Hz</th>
<th>10 kHz</th>
<th>1000 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS(38.1%)</td>
<td>39.7</td>
<td>2.64</td>
<td>0.4</td>
</tr>
<tr>
<td>sSEBS(65.0%)</td>
<td>1440</td>
<td>351.0</td>
<td>7.4</td>
</tr>
<tr>
<td>sSEBS(38.1%)/SrTiO(_3)(13.5%)</td>
<td>49.2</td>
<td>39.1</td>
<td>10.1</td>
</tr>
<tr>
<td>sSEBS(65.0%)/SrTiO(_3)(11.1%)</td>
<td>1380</td>
<td>554.0</td>
<td>37.5</td>
</tr>
</tbody>
</table>

**Table II-16.** Dielectric tan\( \delta \) of sSEBS and sSEBS/SrTiO\(_3\) at Various Frequencies at 20 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>100 Hz</th>
<th>10 kHz</th>
<th>1000 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS(38.1%)</td>
<td>1.33</td>
<td>0.41</td>
<td>0.12</td>
</tr>
<tr>
<td>sSEBS(65.0%)</td>
<td>0.43</td>
<td>2.62</td>
<td>1.20</td>
</tr>
<tr>
<td>sSEBS(38.1%)/SrTiO(_3)(13.5%)</td>
<td>0.24</td>
<td>0.46</td>
<td>1.06</td>
</tr>
<tr>
<td>sSEBS(65.0%)/SrTiO(_3)(11.1%)</td>
<td>0.43</td>
<td>0.76</td>
<td>1.61</td>
</tr>
</tbody>
</table>
The $\varepsilon''$ vs. frequency curves for each sample are seen in Figure II-19 and $\varepsilon''$ values at selected frequencies are listed in Table II-15. The Tan$\delta$ vs. frequency dependence of each samples are compared in Figure II-20. The Tan$\delta$ at given frequencies are listed in Table II-16.

![Graph of $\varepsilon''$ vs. Frequency](image)

**Figure II-19.** Frequency dependence of dielectric constant ($\varepsilon''$) of sSEBS(38.1%), sSEBS(65.0%), sSEBS(38.1%)/SrTiO$_3$(13.5%), and sSEBS(65.0%)/SrTiO$_3$(11.1%) films at 20 °C.

There are some models used for predication of the effective dielectric constant in polymer/ceramic heterogeneous materials for a given filler volume fraction.$^{54,55,56,57}$ For example, Maxwell-Garett approximation is as following equation:

$$
\varepsilon_{\text{eff}} = 1 + \frac{3 f_{\text{in}} \beta}{1 - f_{\text{in}} \beta} \quad \text{Eq. 6}
$$

where $\varepsilon_{\text{eff}}$ is the effective dielectric constant of composites, $f_{\text{in}}$ is the volume fraction of inorganic filler, $\beta = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2 \varepsilon_1)$; $\varepsilon_1$ and $\varepsilon_2$ are the dielectric permittivity of polymer matrix and inorganic fillers.
**Figure II-20.** Frequency dependence of dielectric tanδ of sSEBS(38.1%), sSEBS(65.0%), sSEBS(38.1%)/SrTiO$_3$(13.5%), and sSEBS(65.0%)/SrTiO$_3$(11.1%) films at 20 °C.

However, for these sSEBS/SrTiO$_3$ films it is difficult to predict effective dielectric constants for them using those models. Our sSEBS/SrTiO$_3$ films are complicated heterogeneous system, containing ionic polymer matrix, metal cations (Sr and Na cations), SrTiO$_3$ particles. Meanwhile, the dc conductivity and strong interfacial polarization may contribute to the dielectric properties. Furthermore, the volume fraction in situ formed SrTiO$_3$ in nanocomposites is hard to estimate.

**Conclusions**

Crystalline SrTiO$_3$ nanoparticles were successfully synthesized within preformed sulfonated, mesophase separated SEBS film templates. Elemental composition analysis by ESEM/EDX showed an essentially uniform concentration of SrTiO$_3$ along the composite film thickness direction, which is beneficial in an applications context. It was
demonstrated that the growth and final morphology of the SrTiO₃ nanoparticles was influenced by the morphology of the of the polymer template. AFM images indicated that the sSEBS matrix in sSEBS/SrTiO₃ hybrids retained the same lamellar morphology as that of the pure sSEBS film. The template effect of was further supported by the observation of nanocomposite morphology in which clusters of SrTiO₃ rods were inserted oriented along hydrophilic domains suggested by comparison of lamellar morphology in AFM images and SrTiO₃ clusters in TEM micrographs. The selected area electron diffraction results further confirm in situ formation of crystalline SrTiO₃ inside sSEBS films and showed highly crystalline structures. In the characterization of dielectric properties, introduction of SrTiO₃ adjusted the dielectric permittivity and its frequency dependence in a positive way in relation to extreme dielectric materials in energy storage and conversion devices.

Acknowledgments

The authors gratefully acknowledge the ACS Petroleum Research Fund (PRF #43754-AC7) for their support. The authors also thank Dr. Andreas Plagge in Polymer Department for his assistance in characterization with TEM/EDX/SAED, and Dr. Michael Blanton in Polymer Department for his assistance in characterization with ESEM/EDX.
Bibliography


CHAPTER III

MORPHOLOGY AND TRANSPORT PROPERTIES OF SULFONATED POLY[STYRENE-B-(ETHYLENE-CO-BUTYLENE)-B-STYRENE]/SILICATE NANOCOMPOSITE MEMBRANES

Abstract

Model nanocomposite proton exchange membranes were prepared via in situ sol-gel reactions of tetraethylorthosilicate (TEOS) in sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene] (sSEBS) solutions that were solution cast into films. The silicate content was measured by thermogravimetric analysis. Mechanical properties of membranes were improved by introduction of silicate nanoparticles. These hybrid membranes exhibited nanophase separated morphology with the particles mainly dispersed in the hydrophilic sulfonated block domains as seen using atomic force microscopy. Water vapor sorption isotherms were generated and it was seen that the number of water molecules per sulfonic acid group increased with silicate content. Some sSEBS/silicate membranes exhibited lower methanol permeability than Nafion® 117 while others showed higher methanol permeability. Methanol permeability increased with introduction of silicate which was attributed to the broadening of hydrophilic domains by silicate insertion. Proton conductivity increase in membranes containing around 10wt% silicate is discussed in terms of the morphological change and synergetic effect by silicate particles.

Introduction

Direct methanol fuel cells (DMFCs), which can be made into compact and lightweight sizes, have the advantages of higher energy density than current rechargeable
lithium battery and more convenience.\textsuperscript{1} Due to these advantages, DMFCs have been identified as one of the most promising alternative to current power resources for portable electronic devices.\textsuperscript{2} To realize large scale commercialization, DMFCs are expected to meet the requirements of power efficiency, durability and cost. As a critical component in DMFCs, polymer electrolyte membranes (PEMs) have attracted a great deal of research interest. Ideal PEMs should have high proton conductivity and low methanol crossover to obtain high power density and high efficiency as well as good stability and durability and low cost for commercialization.\textsuperscript{3,4} The search for new PEM types has continued to be an active area of research in order to improve their performance and enable the commercialization of DMFCs.\textsuperscript{5,6,7,8} A wide variety of polymer membranes have been studied as PEM candidates including fluorinated ionomers (Nafion\textsuperscript{®}, Flemion\textsuperscript{®})\textsuperscript{9,10}, sulfonated hydrocarbon polymers such as poly(ether-ether-ketone) (PEEK), poly(arylene-ether-sulfone) (PAES), polyimides, polybenzimidazole,\textsuperscript{11,12,13,14,15} polymer blends\textsuperscript{16,17} and polymer-inorganic composites.\textsuperscript{18,19} However, it is still a challenge to achieve a membrane with good balance of critical properties such as high proton conductivity, low methanol crossover, good mechanical properties and affordable cost.\textsuperscript{20,21} Synthesis of polymer membranes with high ion exchange capacity (IEC) can improve proton conductivity but very high water uptake caused by high IEC may result in poor membrane mechanical properties and low physical and chemical durability in the fuel cell environment.

Membranes consisting of a polymer matrix with inorganic inclusion may improve the critical properties and in the sense of optimization.\textsuperscript{22,23,24,25,26,27} Recent research in polymer-inorganic membranes demonstrated improvements such as higher conductivity,
better mechanical properties and lower methanol crossover.\textsuperscript{18} Sulfonated poly(ether-ether-ketone)/ZrO\textsubscript{2} composite membranes exhibited reduced methanol crossover than the pure polymer membranes.\textsuperscript{18} The addition of zirconium hydrogen phosphate into sulfonated PAES membranes improved mechanical properties while reducing methanol crossover relative to the pure polymer membranes.\textsuperscript{26} Most polymers have been studied for polymer-inorganic composites, including Nafion\textsuperscript{®}, sulfonated PAES and sulfonated PEEK, while the inorganic phases were SiO\textsubscript{2}, ZrO\textsubscript{2}, TiO\textsubscript{2}, clays, Montmorillonite (MMT), zeolite, and zirconium phosphate.\textsuperscript{28} Preparation of composite membranes are mainly classified into three approaches.\textsuperscript{29} In the first, inorganic particles (or powder) are mixed into a polymer dispersion or solution followed by film casting and solvent removal. The main problem in this method is possible particle aggregation. In the second method, inorganic precursor monomers permeate into pre-formed polymer membranes; the absorbed precursors react in situ to form inorganic particles.\textsuperscript{30} Mauritz et al. studied the formation of various metal oxides (SiO\textsubscript{2}, TiO\textsubscript{2}, ZrO\textsubscript{2}) in different polymer films including Nafion\textsuperscript{®} and other sulfonated polymers.\textsuperscript{31,32,33,34,35} In the third method of composite preparation, inorganic precursors are firstly mixed in a polymer solution to create a dispersion and the reaction of precursors takes place throughout the polymer solution medium to form the inorganic nanoparticles. The composite membranes are then created by casting films of these multi-component mixtures with the removal of solvent.\textsuperscript{36,37,38,39} Although there has been extensive research of polymer/inorganic composite membranes as PEMs, most polymer matrices are based on homopolymers or random copolymers while few are based on the block copolymers discussed here.
The morphology and microstructure of membranes influence their proton conductivity, water uptake and mechanical properties.\textsuperscript{40,41,42} The morphology of Nafion\textsuperscript{®} and sulfonated poly(ether-ketone) (sPEK) was compared by Kreuer who discussed that the semicrystalline structure and continuous ionic channels of Nafion\textsuperscript{®} contribute to the greater proton conductivity than sPEK.\textsuperscript{43} McGrath et al. compared their block copolymers with random copolymers, namely, multiblock copolymers consisting of sulfonated poly(arylene ether sulfone) and fluorinated poly(arylene ether) blocks. They showed that the blocky structures had greater conductivity than the corresponding random copolymers which was attributing to the well defined phase separation in the former.\textsuperscript{44,45}

Block copolymer membranes are also superior to random copolymer membranes in mechanical properties and dimension stability. For random copolymer membranes, high IEC usually lead to very high water swelling and poor mechanical properties.\textsuperscript{46,47} In block copolymer membranes, hydrophobic domains provide mechanical strength while hydrophilic domains form interconnected proton transport channels under hydration. Sulfonated poly[styrene-b-(ethylene-co-butylene)-b-styrene] (sSEBS) triblock copolymers have received interest as a block copolymer for PEMs because of its low cost.\textsuperscript{48,49,50} As a typical A-B-The mesophase separated morphology of sSEBS offers opportunities to improve properties related to PEMs. In Kim’s studies, sSEBS membranes with sulfonation degree greater than 30\% showed close proton conductivity to Nafion\textsuperscript{®} 117 and smaller methanol permeability.\textsuperscript{48} In another study sSEBS membranes with the same sulfonation degree showed different proton conductivities and methanol permeability depending on their morphologies affected by using different casting
solvents. Owing to better interconnectivity of ion channels, sSEBS with disordered and frustrated morphologies exhibited both higher proton conductivity and methanol permeability than sSEBS having ordered lamellar structures. One concern of sSEBS from Kim’s SAXS study was that the sulfonated polystyrene domains showed greater interaction with methanol than water.\(^{50}\)

Tetraethylorthosilicate (TEOS) is one of the most common sol-gel reaction precursor.\(^{51}\) Silicate particles can be prepared from TEOS by hydrolysis followed by polycondensation reactions. The Mauritz group performed much research on the synthesis and characterization of nanocomposite membranes consisted of Nafion\(^{®}\) and other sulfonated polymers using the second and third composite membrane preparation methods.\(^{30}\) In the second method, preformed polymer films were used as templates and hydrolyzed TEOS polar monomers selectively migrated into the hydrophilic domains in which polycondensation reactions proceed to form silicate nanoparticles. The phase separation morphology plays an important role in controlling of particle size and distribution. In the third method, TEOS was mixed in solutions of sulfonated poly(styrene-b-ethylene-co-butylene-b-styrene) (sSEBS) and hydrolysis and polycondensation of TEOS occur in polymer solutions, followed by solution casting. Morphological studies of sSEBS/silicate showed that silicate particles of nanometer sizes disperse evenly mainly in sulfonated styrene domains. This result suggested that the self assembly of hydrophilic and hydrophobic blocks occurs and that silicate particle size was controlled by the hydrophilic domains. There were some studies of polymer/inorganic composite membranes as PEMs based on Nafion\(^{®}\) or other random copolymers.\(^{52,53}\) However, little
was studied about the influence of silicate inclusion on morphology and transport properties of block copolymer/inorganic composite membranes.\textsuperscript{54}

In this paper, we will employ the third method to synthesize sSEBS/silicate membranes via in situ sol-gel reaction of TEOS in sSEBS solution followed by solution casting of films. One major difference from previous work in our group is that the sSEBS employed will have higher sulfonation degrees, and the loading of silicate was increased to see the effect of silicate at a wide loading range. The introduction of silicate particles in hydrophilic domains are expected to improve membrane dimension stability and reduce methanol permeation. Thermal stability and mechanical properties will be characterized by TGA and MTS. Water uptake, methanol permeability and proton conductivity was studied and related to the morphologies identified with AFM. The effect of parameters such as sulfonation degree and silicate loading on membrane properties were studied. Structure-property relationships will be discussed based on morphology observations. This research is meaningful because nanocomposite membranes not only have the potential to improve fuel cell PEMs by the combination of block copolymer matrix and inorganic inclusion, but also provide good opportunity to study structure-property relationships.

Experimental

Materials

Poly[styrene-\textit{b}-(ethylene-\textit{ran}-butylene)-\textit{b}-styrene] (SEBS) triblock copolymers were obtained from Kraton® LLC. The samples have $M_n \sim 48,000$ g·mol$^{-1}$ and a polydispersity index of ~1.04 as determined by GPC and a styrene block weight content of ~30% as determined by $^1$H NMR spectroscopy. Toluene, isobutanol, 1,2-
dichloroethane (DCE) (99.8%), acetic anhydride (ACS grade), sulfuric acid (ACS grade) and TEOS (98%) were obtained from Fisher Co. and used without further purification. Nafion® 117 membranes obtained from E. I. DuPont Co. were cleaned by boiling in 8M nitric acid for 2h followed by boiling in deionized water twice for 2h to leach out residuals. The membranes were then dried at 100 °C under vacuum for 24h.

**Sulfonation of SEBS**

SEBS was sulfonated with acetyl sulfate according to the procedure reported by Mauritz et al. SEBS was dissolved in DCE at 50 °C. The sulfonating agent, acetyl sulfate, was generated by addition of sulfuric acid to a solution of acetic anhydride in DCE. The amount of acetyl sulfate required for the desired level of sulfonation was added to the polymer solution. The reaction proceeded for ~ 3-4 h and polymer was recovered by steam stripping. The sSEBS was dried under vacuum at 50 °C for longer than 5 days until constant mass was achieved. Membranes of the sSEBS were prepared from casting of toluene/isobutanol (or toluene/hexanol) co-solvent solution into Teflon dishes and allowed to dry at 50 °C for 5 days followed by annealing under vacuum at 120 °C for 2 days.

**Preparation of sSEBS/Silicate Membranes**

sSEBS samples were dissolved in a mixed solvent of toluene/isobutanol (or toluene/hexanol) with the volume ratio of 85/15 at the concentration 3-5% (w/v). The desired amount of TEOS and DI water (containing 0.15 M HCl catalyst) with the stoichiometric ratio (4:1) of H2O-to-(Si-OR) was added to the polymer solution and stirred for 4h at room temperature. Films of the hybrid materials were cast from the above reactive solutions in the fashion as described for the sulfonated SEBS membranes. All
membranes have thicknesses in the range 0.1-0.3 mm. The weight ratios of polymer and TEOS in the reaction solution were recorded in Table III-1.

**Table III-1.** Ratio of Polymer and TEOS in Membrane Preparation and Silicate Content in Dry Membranes

<table>
<thead>
<tr>
<th>Serial name</th>
<th>Membrane name</th>
<th>Polymer (wt%)</th>
<th>TEOS (wt%)</th>
<th>Silicate (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS (19.3%)/silicate</td>
<td>sSEBS (19.3%)/silicate (9.8%)</td>
<td>74.2</td>
<td>25.8</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>sSEBS (19.3%)/silicate (19.9%)</td>
<td>53.5</td>
<td>46.5</td>
<td>19.9</td>
</tr>
<tr>
<td>sSEBS (19.3%)/silicate (25.0%)</td>
<td>41.9</td>
<td>58.1</td>
<td>25.0</td>
<td></td>
</tr>
<tr>
<td>sSEBS (38.1%)/silicate</td>
<td>sSEBS (38.1%)/silicate (7.8%)</td>
<td>74.2</td>
<td>25.8</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>sSEBS (38.1%)/silicate (17.3%)</td>
<td>53.5</td>
<td>46.5</td>
<td>17.3</td>
</tr>
<tr>
<td>sSEBS (38.1%)/silicate (24.5%)</td>
<td>41.9</td>
<td>58.1</td>
<td>24.5</td>
<td></td>
</tr>
<tr>
<td>sSEBS (63.8%)/silicate</td>
<td>sSEBS (63.8%)/silicate (8.6%)</td>
<td>75.4</td>
<td>24.6</td>
<td>8.6</td>
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<tr>
<td></td>
<td>sSEBS (63.8%)/silicate (18.8%)</td>
<td>55.1</td>
<td>44.9</td>
<td>18.8</td>
</tr>
<tr>
<td>sSEBS (63.8%)/silicate (26.3%)</td>
<td>43.4</td>
<td>56.6</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>sSEBS (76.2%)/silicate</td>
<td>sSEBS (76.2%)/silicate (7.6%)</td>
<td>74.2</td>
<td>25.8</td>
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<td>46.5</td>
<td>17.3</td>
</tr>
<tr>
<td>sSEBS (76.2%)/silicate (23.0%)</td>
<td>41.9</td>
<td>58.1</td>
<td>23.0</td>
<td></td>
</tr>
</tbody>
</table>

**Membrane Characterization**

*Sulfonation degree (SD) and ion exchange capacity (IEC).* sSEBS sulfonation level was determined by titration. Samples were dissolved in a toluene/hexanol (85/15 volume ratio) mixture with a concentration of ~0.2 - 0.4 g/mL. This solution was titrated against 0.05 M NaOH standard solution in methanol to a phenolphthalein endpoint. The normality of the standard solution was determined by 0.01 M p-toluene sulfonic acid in methanol. The degree of sulfonation, x%, is the mole percent of styrene units sulfonated; each sulfonated sample is denoted as sSEBS(x%). The ion exchange capacity (IEC) was calculated from titration results of sSEBS in Table 2.

*Thermal stability.* A TA Instruments Thermogravimetric Analyzer Q50 was used in analyzing samples of 4-13 mg which were heated from 30 to 700 °C at 10 °C/min under a N₂ environment with a flow rate 60 mL/min. Silicate contents for each sample
were calculated as the difference in percent char between the filled membrane and corresponding pure sSEBS matrix.

**Mechanical property.** Uniaxial tensile testing was performed using an MTS Alliance RT/10 tensile setup equipped with a 100 N load cell. All membranes were cut into ASTM standard dog bone specimens with a gauge length of 31.0 mm and a width of 2.94 mm. The specimens were tested at a constant stretching speed of 10 mm/min under ambient conditions (ca. 23 °C and 40% relative humidity).

**Membrane morphology.** Tapping mode atomic force microscopy (TM-AFM) phase images were obtained using a Digital Instruments Dimension 3000 scanning probe microscope at ambient conditions. Cross-sections of samples for AFM observation were prepared by cryo-microtoming sample films using a diamond knife at -110 °C in order to create a smooth surface. All samples were equilibrated at 40% relative humidity (RH) for at least 24h before being imaged immediately at room temperature. In tapping mode, a cantilever holding a responsive silicon tip was rastered across the surface at a particular rate while the tip taps on the surface with a certain frequency. Phase images are created on the basis of the phase difference between the input and output responses of the cantilever. This provides a qualitative measure of the local viscoelastic properties in the vicinity of the tip. Because of the large difference between the viscoelastic properties of the hard and soft block domains in samples at room temperature, significant contrast can be generated in a phase image to allow for observation of morphology.55,56

**Water vapor uptake.** Moisture content was measured vs. RH at 80 °C in the order of decreasing RH, using a TA Instruments Q5000 SA sorption analyzer. A weighed sample that was equilibrated at RH = 90% at 80 °C was then dried in the instrument and
exposed to a series of humidity step changes at 80 °C from high to low RH. At a given
step, the RH was held constant until the weight change was undetected within one hour
and the water uptake was calculated from the weight loss of hydrated membranes during
this stepwise desorption process. Water weight uptake and the number of moles of water
per sulfonic acid group (\( \lambda \)) were calculated using Equations 1 and 2.

\[
Water \text{ uptake (wt\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]

\[
\lambda = \frac{\text{moles of water}}{\text{moles of acid groups}}
\]

*Methanol permeability.* The rate of passage of methanol through these
membranes was studied using a temperature regulated side-by-side glass permeation cell
(PermeGear) in conjunction with an in-line FTIR-ATR spectrometer that detected
chemical groups in the permeant molecule.\(^{57}\) The spectrometer (Bruker Equinox 55) was
equipped with a flow-through liquid cell that was mounted on a single reflection,
horizontal ATR accessory (Harrick Scientific Products). A zinc selenide crystal was used
in the ATR accessory.

The permeation cell consists of two liquid compartments separated by the
membrane under test. Samples were hydrated in DI water for 48h prior to measurement,
after which they were clamped between the two compartments in which the liquids were
stirred throughout the experiment. One compartment (A) contained an aqueous 2M
methanol solution and the other compartment (B) contained DI water that was pure in the
beginning of the experiment. The methanol in reservoir A was absorbed into the
membrane, diffuses to the opposite side under a concentration gradient, and enters the
liquid in compartment B. The B solution was circulated by a low flow pump to an in-line
FTIR-ATR spectrometer in a flow-through liquid cell that detected methanol concentration. The methanol concentration in B was continuously detected by FTIR throughout each experiment at 4 min time intervals with the signal averaging 128 scans at a resolution of 4 cm\(^{-1}\). The infrared absorbance peak at 1016 cm\(^{-1}\) that represents the C-O stretching vibration of methanol was tracked and related to the methanol concentration.

The methanol concentration in compartment B was calculated by calibration with standard methanol aqueous solution with given concentration via Beer’s Law. The following approximation equation was used to describe the increase of methanol concentration in time (t) in compartment B at early times:

\[
C_B(t) = \frac{PC_AA}{V_BL}(t - \frac{L^2}{6D})
\]

(3)

\(C_A\) is the methanol concentration in the donor compartment and the equation holds under the condition \(C_A \gg C_B\). \(L\) is the membrane thickness, \(A\) the membrane cross-sectional area and \(V_B\) the solution volume in compartment B. When equation 3 is rearranged as follows, the slope of a linear section on a \([C_B(t)V_BL]/(C_AA)\] vs. \(t\) graph gives \(P\).

\[
\frac{C_B(t)V_BL}{C_AA} = P(t - \frac{L^2}{6D})
\]

(4)

A lag time, \(t_e\), can be obtained by back-extrapolating the fitted line to the time axis. Knowing \(t_e\) and \(L\), an ‘early time’ diffusion coefficient can be calculated by using following equation:

\[
D = \frac{L^2}{6t_e}
\]

(5)

**Proton conductivity.** In-plane proton conductivity was measured using a four-point probe electrode configuration in a BekkTech BT-512 Membrane Conductivity Test System. All stored membranes were not hydrated before measurement. During the
measurement, a given membrane sample (dimensions ~ 5 mm x 25 mm) was placed in a conductivity cell in which the temperature and humidity were controlled. Proton conductivities were measured at 80 °C and as membrane samples being exposed to a series of relative humidity environments with RH increasing from 20 to 100% in step of 10%. To track possible huge change of proton conductivity at some RH, additional conductivity data at RH of 25% and 95% were particularly recorded. The electrical resistance ($R$) of a sample was calculated via Ohm’s law using a least squares fit of the voltage-current data by the instrument software. Proton conductivity was then calculated by using the following equation:

$$\sigma = \frac{L}{R \times W \times T}$$

where $\sigma$ is the conductivity, $L$ is the distance between the two central electrodes in the conductivity cell, $W$ is the width of the sample, and is $T$ the sample thickness.

Results and Discussion

**Preparation of sSEBS/Silicate Composite Membranes**

Sulfonated SEBSs with various sulfonated degrees were employed in preparation of composite membranes. The weight ratio of sSEBS and silicate precursor TEOS were listed in Table 1. The silicate content in final composite membranes was calculated based by remained char difference between composite membranes and relevant pure sSEBS film based on TGA results (Table 1).

**Ion Exchange Capacity and Sulfonation Degree**

The ion exchange capacity (IEC) and sulfonation degree (SD) of each sulfonated SEBS membrane (before silicate modification) was calculated from the titration results listed in Table III-2. In calculating SD, the effect of molecular weight increase of sSEBS
after sulfonation should be considered especially at high sulfonation degrees. For example, SD is 55.0% for sSEBS (63.8%) if the increase in molecular weight is not considered.

**Table III-2.** Sulfonation Degree and Ion Exchange Capacity of sSEBS Membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>SD (%)</th>
<th>IEC (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS (9.6%)</td>
<td>9.3</td>
<td>0.27</td>
</tr>
<tr>
<td>sSEBS (19.3%)</td>
<td>19.3</td>
<td>0.54</td>
</tr>
<tr>
<td>sSEBS (38.1%)</td>
<td>38.1</td>
<td>1.01</td>
</tr>
<tr>
<td>sSEBS (63.8%)</td>
<td>63.8</td>
<td>1.61</td>
</tr>
<tr>
<td>sSEBS (76.2%)</td>
<td>76.2</td>
<td>1.87</td>
</tr>
</tbody>
</table>

**Thermal Degradation**

TGA thermograms provided thermal stability of sSEBS/silicate membranes. In Figure III-1, the weight loss curves of sulfonated SEBS exhibit four distinct degradation events while unsulfonated SEBS mainly shows one event. Four weight loss stages are seen more clearly in the derivative curves in Figure III-2. Weight loss of unsulfonated SEBS occurred in a single process over the temperature range of 400-470 °C which corresponds to the degradation of polymer chains. For sSEBS samples, weight loss occurred in four stages over the temperature ranges of 50-150 °C, 220-370 °C, 370-430 °C and 430-490 °C.
Figure III-1. TGA thermograms of SEBS and sSEBS of indicated sulfonation degrees.

Figure III-2. Derivative TGA curves of SEBS and sSEBS of different sulfonation degrees.
These stages are attributed, sequentially, to release of absorbed moisture, cleavage of sulfonic acid groups attached to styrene rings and decomposition of the styrene and ethylene/butylene blocks.\textsuperscript{58} In comparing SEBS and sSEBS, it was found that the decomposition of polymer chains shifts to higher temperatures with sulfonation. Introduction of silicate components did not greatly affect the thermal behavior of the sSEBS host matrix. Perhaps this is due to the silicate component being highly segregated from the matrix. As illustrated in Figures III-3 and III-4, all sSEBS and sSEBS/silicate samples exhibit four weight loss stages, and the final degradation temperature did not show significant shift with silicate introduction of silicate. This result was also reported in our previous study of sSEBS/silicate hybrid materials in which lightly sulfonated sSEBS was also the matrix.\textsuperscript{55}

\textbf{Figure III-3.} TGA thermograms of sSEBS (55.7\%) and composite membranes.
Figure III-4. Derivative TGA curves of sSEBS (55.7%) and composite membranes.

Mechanical Properties

PEM mechanical properties are important within the context of fuel cell durability under temperature and humidity cycling. These perturbations can lead to craze and pinhole formation in constrained membranes which, in turn, leads to fuel crossover. 59 Tensile stress vs. strain curves for the series of sSEBS (76.2%) membranes with indicated silicate compositions are in Figure III-5. The curves for all sSEBS and sSEBS/silicate samples are linear in the low strain region, display yield followed by plastic deformation, a rise in stress and ultimate rupture. The sSEBS/silicate samples exhibit higher modulus and higher yield stress as well as higher stress levels than pure SEBS, and these characteristics increase with increasing silicate content. Thus, the incorporated silicate structures offer mechanical reinforcement which may be due to strong interfacial interactions or silicate structures that became mixed in the hard blocks domains during
formation. The fact that elongations-at-break were over 400% implies that the sol-gel-grown silicate structures are isolated rather than contiguous. The mechanical tensile parameters extracted from these curves are listed in Table III-3.

![Stress vs. strain graph](image)

**Figure III-5.** Stress vs. strain for sSEBS(76.2%) membranes of indicated silicate compositions.

**Table III-3.** Mechanical Tensile Properties of sSEBS(76.2%)/Silicate Membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial Modulus (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Yield Strain (%)</th>
<th>Ultimate Strength (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sSEBS(76.2%)</td>
<td>91.2</td>
<td>3.5</td>
<td>9.6</td>
<td>8.6</td>
<td>515.7</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(7.6%)</td>
<td>132.6</td>
<td>4.8</td>
<td>11.9</td>
<td>15.2</td>
<td>598.2</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(17.6%)</td>
<td>251.2</td>
<td>6.9</td>
<td>9.4</td>
<td>14.0</td>
<td>519.4</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(23.0%)</td>
<td>251.5</td>
<td>8.2</td>
<td>10.0</td>
<td>13.8</td>
<td>462.9</td>
</tr>
</tbody>
</table>

**Membrane Morphology**

Tapping mode/phase images of sSEBS are displayed in Figure III-6. The dark regions are assigned to the sulfonated polystyrene domains while the bright regions
correspond to the soft ethylene/butylene domains. Normally, for AFM phase images under moderate tapping, the bright regions (having high phase angle) usually correspond to harder domains while dark regions (having low phase angle) correspond to soft domains.\textsuperscript{60,61}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{AfM_images.png}
\caption{Representative AFM tapping/phase images of sulfonated SEBS: a) sSEBS(19.3\%), b) sSEBS(38.1\%), c) sSEBS(63.8\%), and d) sSEBS(76.2\%). The image squares have dimensions 2 μm x 2 μm. a – d phase scale ranges are 0 - 20°, 0 - 50°, 0 - 25° and 0 - 30°, respectively. Dark regions are of sulfonated PS composition.}
\end{figure}

When these sSEBS samples absorb moisture from the atmosphere, the hydrophilic sulfonated polystyrene blocks are expected to hydrate while the hydrophobic
ethylene/butylene blocks will not. This selective hydration may cause local plasticization that renders the sulfonated PS block domains soft. Our assignment is comparable to those in other literature reports that deal with like systems.\textsuperscript{62,63} For example, in the TP-AFM images of sulfonated poly(arylene ether) copolymers, the dark regions in the images were assigned to a soft structure, corresponding to the hydrophilic sulfonated groups containing water. The bright phases in the images were attributed to a hard structure, corresponding to hydrophobic polymer matrix.\textsuperscript{63}

In Figure III-6 the images of all sSEBS samples with varying SD exhibit pronounced microphase separation with characteristic domain sizes in the range 20-30 nm. The well-ordered cylindrical morphology of unmodified SEBS having this S block domain volume fraction is not present.\textsuperscript{64} The hard block phase features are elongated in most cases and isolated, as is expected at this block composition. The vermiculated, worm-like patterns can be described as ‘frustrated’ as reported in earlier similar studies.\textsuperscript{55} Sulfonation increased the polarity of the S blocks which increased the Flory-Huggins interaction parameter, $\chi$, between the blocks. Also, high degrees of sulfonation will increase the volume fraction of S block domain which might affect a morphological shift. In addition to thermodynamics, the effect of the kinetics of morphology development must be considered. In this regard, there will be restrictions on S block segmental mobility due to hydrogen bonding interactions between sulfonic acid groups. These interactions will interfere with the drive toward equilibrium with the result that the observed morphologies are of lower degree of order within the time scale of the film casting experiment. The time that would be required for these materials to attain an equilibrium morphology would need to be found by experiment.
Figure III-7. Representative tapping mode AFM phase images of sSEBS(63.8%)/silicate(8.6%) and sSEBS(63.8%)/silicate(18.8%) samples. Figure squares have dimensions 2 µm x 2 µm, and phase scale ranges for a) and b) are 0-40° and 0-100°, respectively. Dark regions are of sulfonated PS composition.

Figure III-7 shows the heterogeneous morphologies of sSEBS(63.8%)/silicate(8.6%) and sSEBS(63.8%)/silicate(18.8%) samples. It appears in Figure III-7(a) that the frustrated phase separation observed in non-silicate modified sSEBS is also present where the worm-like bright phases correspond to the ethylene/butylene domains and dark regions are sulfonated S block domains. Not present in Figure III-6 but seen in Figure III-7 are well dispersed objects of sizes 50-100 nm that would reasonably seem to be in situ grown silica particles that, on close inspection, appear to be inserted in the dark areas that composed of sulfonated S blocks, as expected. This result reinforces the view that silicate particles preferentially grow in the hydrophilic domains. It appears that such insertion of silicate particles expands the sulfonated S domain sizes while the EB domain sizes remain about the same as those in pure sSEBS.
The morphology, seen in Figure III-7b for a higher silicate loading (18.8%), is dominated by particles whose sizes have increased to 80-150 nm, as expected.

Figure III-8. AFM phase images of sSEBS(76.2%)/silicate(17.3%) and sSEBS(76.2%)/silicate(23%). Figure squares have dimensions 2 µm x 2 µm, and phase scale ranges are 0-70° and 0-140° for a) and b), respectively. Dark regions are of sulfonated PS composition.

Figure III-8 shows the morphologies of sSEBS(76.2%) having (a) 17.3 and (b) 23.0% silicate content. Particles are seen to be dispersed throughout the sSEBS matrices for both loadings. The particles in sSEBS(76.2%)/silicate(17.3%) are on the order of 30-70 nm dimensions while those in sSEBS(76.2%)/silicate(17.3%) are around 40-70 nm, both being smaller than those in the sSEBS(63.8%)/silicate membranes. The white (EB) regions are rather elongated and in places are parallel to each other. This suggests that sSEBS with higher sulfonic acid groups could better restrict the aggregation of silicate particles during the formation. When we focused on the morphologies of sSEBS matrices in Figure 8, we found that sSEBS matrix with higher silicate content showed more
frustrated pattern. This also suggests that during the formation of composite membranes, the interaction between silicates and polymer chains contributed to the final morphology.

**Equilibrium Water Vapor Uptake**

Water vapor sorption at fuel cell operating temperatures and external RH is an important PEM property as relates to proton conductivity. The ability of the membrane to avoid dehydration at temperatures approaching or beyond 100 °C is essential. Mechanical properties, proton conductivity, transport of water and methanol and chemical degradation are dependent on water uptake. Thus, determining the number of water molecules per sulfonic acid group, \( \lambda \), vs. RH at a given temperature is important. The distribution of water molecules into bound and free states can determine the degree to which proton migration occurs along hydrogen bonds of water molecules or between \( \text{SO}_3\text{H} \) groups, although the vapor sorption test does not address this level of complexity. The information from these studies is useful because fuel cell membranes undergo changing humidification in fuel cells.

Weight uptake and \( \lambda \) vs. RH data at 80 °C for sSEBS and, for comparison, for Nafion\textsuperscript{®} 117 are plotted in Figure III-9. As expected, all samples show increased water uptake with increased RH. On the basis of uptake by weight, the curves monotonically elevate, starting from below the curve for N117 until the curves for the two highest SDs are above that for N117. This is simply rationalized in terms of an increasingly greater concentration of fixed hydrophilic acid groups on the outer blocks. When plotted on the basis of moles, \( \lambda \), all of the curves lie beneath that of N117 and the vertical curve displacement is not progressive. sSEBS(38.1%) exhibited greater \( \lambda \) than both sSEBS(63.8%) and sSEBS(76.2%) at a given RH. Perhaps this result is due to a
morphological shift as discussed earlier. The IEC of N117 is 0.91, which is somewhat lower than that of sSEBS(38.1%) (1.01). In Figure III-9a, N 117 showed higher water uptake than sSEBS(38.1%), but lower than that of sSEBS(63.8%) and sSEBS(76.2%). N 117 showed higher $\lambda$ than all sSEBS samples.

Figure III-9. $\lambda$ (molar ratio of $\text{H}_2\text{O}/\text{SO}_3\text{H}$) vs. RH for Nafion® 117 and sSEBS samples with indicated sulfonation degrees. Data was collected in the order of high to low RH (desorption) at 80 °C.
In Figure III-10a it is seen that the sSEBS(63.8%)/silicate percent water uptake vs. RH curves are not separated by much, except at the highest RH values. On the other hand, in Figure III-10b the $\lambda$ vs. RH curves for sSEBS(63.8%) show monotonic upward displacement with increasing silicate percent. This suggests that SiOH groups bind and structure water molecules. Introduction of silicate structures into sSEBS might be thought
to reduce the effective concentration of sulfonic acid groups by blocking or encapsulating these functionalities during the sol-gel reaction. This, in turn, would reduce the water uptake. Apparently this is not the case.

Regarding the effect of silicate on $\lambda$, the sSEBS(35%)/silicate series and sSEBS(65%)/silicate series exhibit the similar increase of $\lambda$ with silicate content. Figure III-11 showed the $\lambda$ of each serial sSEBS/silicate membranes measured at RH of 90% and 80 °C.

![Figure III-11](image)

**Figure III-11.** Dependence of $\lambda$ on silicate content in sSEBS/silicate membranes at RH of 90% at 80 °C.

Similar to sSEBS(63.8%)/silicate membranes, sSEBS(38.1%)/silicate membranes also showed increase of $\lambda$ with silicate content, with the exception of sSEBS(76.2%)/silicate(23.0%) membrane. This result is compatible to above conclusion.
that hydrophilic silicates can help absorb water in composite membranes. With regard to the effect of SD on \( \lambda \) for composite membranes, similar trend was found like that in the comparison of SD effect on \( \lambda \) for pure sSEBS membranes. In comparison of composition membranes with similar silicate content in three serial membranes, sSEBS(38.1%)/silicate membranes showed highest \( \lambda \), followed by sSEBS(63.8%)/silicate membranes, and sSEBS(76.2%)/silicate membranes. An argument for this result is that introduction of silicate particles generate similar morphological change in these composite membranes. Therefore, the composites membranes keep the same trend as pure sSEBS membranes.

**Methanol Permeability**

Permeabilities of membranes were calculated from the equation 4 based on the IR-ATR measurement results. The typical permeation curve of sSEBS(63.8%) membrane was illustrated in Figure III-12.

![Graph](image)

**Figure III-12.** Permeation curve of sSEBS(63.8%) for calculation of permeability.
Table III-4. Methanol Permeability and Proton Conductivity of Nafion® 117 and sSEBS/Silicate Membranes of Indicated Compositions and IEC Values

<table>
<thead>
<tr>
<th>Sample name</th>
<th>IEC (mmol/g)</th>
<th>Membrane Thickness (mm)</th>
<th>Permeability ((10^{-6}\text{cm}^2/\text{s}))</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>0.94</td>
<td>0.177</td>
<td>1.22</td>
<td>130.4</td>
</tr>
<tr>
<td>sSEBS (38.1%)</td>
<td>1.01</td>
<td>0.188</td>
<td>0.17</td>
<td>32.8</td>
</tr>
<tr>
<td>sSEBS (63.8%)</td>
<td>1.61</td>
<td>0.175</td>
<td>0.72</td>
<td>77.2</td>
</tr>
<tr>
<td>sSEBS(63.8%)/silicate(8.6%)</td>
<td>1.47</td>
<td>0.274</td>
<td>1.01</td>
<td>79.8</td>
</tr>
<tr>
<td>sSEBS (63.8%)/silicate(18.8%)</td>
<td>1.31</td>
<td>0.298</td>
<td>1.07</td>
<td>68.0</td>
</tr>
<tr>
<td>sSEBS(76.2%)</td>
<td>1.87</td>
<td>0.130</td>
<td>1.14</td>
<td>65.5</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(7.6%)</td>
<td>1.73</td>
<td>0.130</td>
<td>1.29</td>
<td>57.6</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(17.3%)</td>
<td>1.62</td>
<td>0.251</td>
<td>1.40</td>
<td>76.2</td>
</tr>
<tr>
<td>sSEBS(76.2%)/silicate(23.0%)</td>
<td>1.44</td>
<td>0.166</td>
<td>1.66</td>
<td>52.5</td>
</tr>
</tbody>
</table>

1) Calculated based on SO₃H groups in sSEBS matrix after reduction of silicate.
2) Thickness measured of dry membranes.
3) Measured at room temperature.
4) Measured results at 80 °C under RH of 100%.

The methanol permeabilities of selected membranes, determined according to the procedure discussed above, are listed in Table III-4. The permeability of N117 is \(1.22 \times 10^{-6}\text{ cm}^2/\text{s}\) which is comparable to values of \(1 \sim 1.5 \times 10^{-6}\text{ cm}^2/\text{s}\) reported in literature, although it is understood that comparison with the results of others is complicated by different conditions of sample preparation, history and experimental procedure. The three unfilled sSEBS membranes have lower methanol permeabilities than that of the N117 membrane and they increase with increasing SD. These sample have the lowest of all permeabilities. As for the filled membranes, the permeabilities for the two having SD 63.8% are essentially the same but the three composites having SD = 76.2% have the highest values all of which are higher than that of N117. Moreover, permeability increases with increasing silicate content. The same trend holds for the sSEBS(63.8%)/silicate(8.6%) and sSEBS (63.8%)/silicate(18.8%) membranes. These results would tend to indicate that these silicate structures have an affinity for methanol.
Perhaps this is can be attributed to a strong affinity between MeOH molecules and accessible SiOH groups on the incorporated silicate structures due to hydrogen bonding. The combination of higher SD and higher silicate content does not result in improved, but rather poorer methanol permeability.

Kim et al. compared the morphology of hydrated sSEBS and N117 derived from small angle X-ray scattering and small angle neutron scattering techniques and found that fully hydrated N117 has average water cluster spacings of 27.3 nm which is much larger than the domain size of sulfonated polystyrene block domains (19.2 nm) in hydrated sSEBS. It was suggested that wide hydrophilic ionic channels in N117 allowed for more facile methanol permeation. The small size of ionic channels in hydrated sSEBS is attributed to the disordered nature of mesophase separation. This would explain why, for unfilled sSEBS, higher IEC translates into increased methanol permeability. It might be thought that introduction of silicate would reduce methanol permeation by increased transport tortuosity but this is not the case as seen in Table III-4. On comparing the morphologies of sSEBS(63.8%) and sSEBS(63.8%)/silicate composite membranes, that hydrophilic domains (dark regions) are seen to be broadened by silicate particles. The interconnected broader channels may explain why permeability was increased with silicate introduction. The similar trend of permeability is also found in the sSEBS(76.2%)/silicate series of membranes. In Figure III-8, sSEBS(76.2%)/silicate(23.0%) showed broader hydrophilic channels than those of sSEBS(76.2%)/silicate(17.3%).

Proton Conductivity
Membrane proton conductivity was determined over a wide range of RH at 80 °C and the results are seen in Figure III-13.

**Figure III-13.** Proton conductivity vs. RH at 80 °C for indicated sulfonation degrees.

The sample with lowest SD (38.1%) has the lowest conductivity, as is reasonable, but the curve for SD = 63.8% is above that for 76.2% despite the proton concentration being higher for the latter. It is noted in Figure III-9 that the $\lambda$ vs. RH curve for 63.8% is above that for 76.2%, as well, so that greater conductivity follows from greater hydration. It should be appreciated that factors beyond IEC and hydration degree, in particular morphology shifting, may cause the conductivity to exhibit non-monotonic behavior.

Morphology is a hidden variable in these tests of macroscopic properties. A comparison of In fact, Figures III-6c and d show that the phase separated morphology of sSEBS(63.8%) is on a finer level such that the widths of the elongated sulfonated S block domains (black) are smaller than those in sSEBS(76.2%). This, in itself, would argue
that the conductivity of sSEBS(76.2%) should be the higher, but close inspection shows that the hydrophilic sulfonated S block phase domains in sSEBS(63.8%) have greater interconnectivity that would contribute to higher proton conductivity. Moreover, these extended domains in many locations appear to be somewhat parallel to each other whereas the sSEBS(76.2%) morphology is less ordered. In Figure III-13, all sSEBS membranes showed lower conductivity than Nafion® 117. This might be due in a general sense to the low values of $\lambda$ for these samples although, on a finer level, the distribution of water molecules into different states of free and bound, as well as variable morphology, must be taken into consideration.

![Proton Conductivity vs. RH at 80°C](image)

*Figure III-14.* Proton conductivity vs. RH at 80°C for sSEBS(63.8%) having indicated silicate compositions.
Figure III-15. Proton conductivity vs. RH at 80 °C for sSEBS(76.2%) having indicated silicate compositions.

Figure III-16. Proton conductivity vs. silicate composition of each sSEBS/silicate membrane at 80 °C and RH of 100%.
Figures III-14 and III-15, and their comparisons with Figure III-13, suggest that introduction of silicate structures into sSEBS reduces proton conductivity. This cannot be due to a reduction in the effective concentration of accessible sulfonic acid groups as the IEC does not decrease with increase in silicate concentration as seen in Table III-4. Increased tortuosity due to silicate structures that pose obstacles to proton migration is worthy of consideration. In Figure III-14, all of the curves except that for 26.3% silicate are essentially the same for practical purposes. All the curves in Figure III-15 for 76.2% silicate are not highly differentiable, as well. The influence of silicate content on proton conductivity at RH of 100% is plotted in Figure III-16. For sSEBS(63.8%)/silicate serial nanocomposite membranes, membranes with silicate content of 8.6% showed the highest conductivity. In other two serial membranes, sSEBS(73.2%)/silicate membranes with silicate content of 7.6% and sSEBS(38.1%)/silicate membranes showed the highest conductivity respectively. The similar trends of proton conductivity in three serial sSEBS/silicate membranes could be attributed to the effect of silicate particles.

Generally, the influence of silicate particles on proton conductivities can be classified into up-effect and down-effect. The down-effect resulted from the reduction of acid concentration due to increase in silicate content and entrapped acid groups in cage effect. The cage effect was verified in Nafion/silicate membranes in our previous study. The up-effect from silicate particles comprises two aspects. Silicate particles with OH groups on surface are hydrophilic and absorb water molecules. In the first aspect, the synergistic effect between the hydrated sulfonic acid group and the hydrated silicate particles can improve the transport of protons. In the second aspect, the introduction of silicate broadened the hydrophilic ionic channels. As we can see from Fig III-7 and III-8, due to
the size of silicate particles are greater than sulfonic acid domains in pure sSEBS (Figure III-6), the dark region surrounding particles represented broadened ionic domains, which improve the connectivity of ionic clusters under hydration. The argument is also supported by the research of Adjemian et al.\textsuperscript{71} In their research of Nafion/silica composite membranes, larger ionic clusters were inferred from SAXS analysis results. At low silicate content, the up-effect was dominant, thus higher conductivity was obtained. With increase of silicate content, the down-effect became dominant, driving conductivity down. It’s possible to obtain higher proton conductivity by optimizing the silicate content in the future.

Conclusions

sSEBS/silicate nanocomposite membranes were prepared via in situ sol-gel reactions of TEOS in polymer solutions that were cast into films. In situ silicate particle formation was controlled by interactions between silicate precursor molecules and the sulfonated polystyrene blocks and the particles were preferentially inserted in the hydrophilic domains while the mesophase separation the block copolymer persisted. Mechanical reinforcement was increased with increased silicate content. Increase in the number of water molecules per sulfonic acid group with silicate content suggests that silicate particles are hydrophilic and help to absorb water molecules. Morphological images revealed that the hydrophilic domains in sSEBS matrices were broadened by insertion of silicate particles, which, in turn, seems to increase methanol permeability. sSEBS/silicate membranes with silicate content around 10wt% showed higher proton conductivity than pure sSEBS membranes, owing to cluster size increase and a synergetic effect between ionic domains and silicate particles. At relatively high silicate contents of
sSEBS/silicate membranes showed decreased conductivity mainly due to reduction of sulfonic acid group concentration, or group dilution. Methanol permeability and proton conductivity were seen to depend on morphological characteristics. It is concluded that [block copolymer]/[inorganic oxide] membranes of this sort are good model systems for fuel cell membranes where the critical properties can be manipulated with morphology.

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CHAPTER IV

MACROMOLECULAR DYNAMICS OF SULFONATED POLY[STYRENE-B-(ETHYLENE-CO-BUTYLENE)-B-STYRENE] BLOCK COPOLYMERS BY BROADBAND DIELECTRIC SPECTROSCOPY

Abstract

Macromolecular dynamics of sulfonated poly[styrene-\(b\)-ethylene-co-butylene]-\(b\)-styrene] (sSEBS) block copolymers were investigated using broadband dielectric spectroscopy (BDS). Two main relaxations corresponding to the glass transitions in the EB and S block phases were identified and their temperature dependences were VFT-like. \(T_g\) for the S block phase shifted to higher temperature due to restrictions on chain mobility caused by hydrogen bonded SO\(3\)H groups. While the EB block phase \(T_g\) appeared to remain constant with degree of sulfonation in DMA experiments, it shifted somewhat upward in BDS spectra. A low temperature relaxation beneath the glass transition of the EB block phase was attributed to short range chain motions. The Kramers-Krönig integral transformation was used to calculate conductivity-free loss permittivity spectra from real permittivity spectra to enhance true relaxation peaks. A loss permittivity peak tentatively assigned to relaxation of internal S|EB interfacial polarization was seen at temperatures above the S block phase glass transition, and the temperature dependence of relaxation was VFT-like. The fragilities of the EB and S block domains in sulfonated SEBS decreased after sulfonation. The temperature dependence of the dc conduction contribution to sSEBS loss spectra also followed VFT-like behavior and S block segmental relaxation time correlated well with conductivity according to the fractional Debye-Stokes-Einstein equation.
Introduction

Block copolymers (BCPs) are phase separated due to a sufficiently large Flory-Huggins interaction parameter and with sufficient block mobility for this self-assembly, with phase geometry determined by block volume fraction. Poly[styrene-\textit{b-}(ethylene-co-butylene)-\textit{b-}styrene] (SEBS) triblock copolymers are useful commercial thermoplastic elastomers owing to the rubbery nature of the inner blocks and mechanical strength offered by the hard block domains that act in similar fashion to cross links.\textsuperscript{1} The thermally reversible hard block domains allow for conventional thermoplastic processing and recycling. SEBS can be functionalized by sulfonation of the styrene (S) blocks.\textsuperscript{2,3} Incorporation of acid groups significantly increases the polarity of the S block domains.

Blackwell and Mauritz performed TEM studies of sulfonated SEBS films cast from solutions of lightly sulfonated SEBS. The micrographs depict distinct two-phase morphologies in which PS domains are dispersed in a continuous EB phase.\textsuperscript{4} Sulfonation influences morphology because strong hydrogen bonding between acid groups slows the kinetics of the evolution of equilibrium morphologies; which, in turn, leads to frustrated morphologies having lesser degrees of long range order. Solution cast SEBS with 14\% sulfonation degree exhibited lamellar morphology with inter-domain spacing of ~ 20-30 nm whereas the unsulfonated control possessed highly ordered cylindrical morphology. SAXS analysis of sSEBS ionomers revealed three phases: an EB soft phase, an S-rich phase and ionic clusters (3-4 nm) dispersed in the PS block domains (20-30 nm).\textsuperscript{3}

Broadband dielectric spectroscopy (BDS) is a powerful tool for interrogating macromolecular dynamics over a wide range of time and distance scales at different temperatures owing to the broad range of frequency ($\nu$) of applied sinusoidal signals.\textsuperscript{5}
For polymers with mobile charges, dc conductivity and its coupling to polymer relaxations can be determined, as well. Phase separated polymers have an additional complication by way of interfaces across which there are gradients of dielectric permittivity and conductivity. Sulfonated SEBS has all of these features and the coupling between them is of great interest with regard to the use of these or similar heterogeneous materials as selective transport media.

**Experimental**

**Materials**

All reagents were used without further purification. The SEBS tri-block copolymer, Kraton® of G1652M grade, was obtained from Kraton® LLC. $M_n$ was ~48,000 g/mol, the polydispersity index was ~ 1.04 (by GPC), and the styrene block content was ~30 wt% as determined from $^1$H NMR. Toluene, isobutanol, 1,2-dichloroethane (DCE) (99.8%), acetic anhydride (ACS grade), and sulfuric acid (ACS grade) were obtained from Fisher Co.

**Sulfonation of SEBS**

SEBS was sulfonated according to the procedure reported by Mauritz et al. SEBS was dissolved in DCE at 50 °C. The sulfonating agent, acetyl sulfate, was generated by addition of sulfuric acid to a solution of acetic anhydride in DCE. The amount of acetyl sulfate required for the desired level of sulfonation was added to the polymer solution. The reaction proceeded for ~3-4 h and the polymer was recovered by steam stripping. The sSEBS sample was dried under vacuum at 50 °C for longer than 5 d until constant mass was achieved. The sulfonation level of sSEBS was determined by titration. The sulfonated samples were dissolved in a toluene/hexanol (85/15 volume ratio) mixture.
with a concentration of 0.2~0.4% g/mL. This solution was titrated against 0.05M NaOH standard solution in methanol to a phenolphthalein endpoint. The normality of the standard solution was determined by 0.01 M \( p \)-toluene sulfonic acid in methanol. The degree of sulfonation (x\%) is the molar percentage of styrene repeat units sulfonated; each sulfonated sample is denoted as sSEBS(x\%).

**Dynamic Mechanical Analysis (DMA)**

Dynamic mechanical properties in tensile mode were acquired using a TA Q-800 dynamic mechanical analyzer, at a frequency of 1 Hz over a temperature range from -120 to + 200 °C with a heating rate of 2 °C/min. The storage modulus (\( E' \)), loss modulus (\( E'' \)), and loss tangent, \( \tan \delta = E''/E' \) were measured as a function of temperature at this frequency. The specimen films were cast from a solution of polymer dissolved in toluene/isobutanol mixture into Teflon dishes, followed by drying at 50 °C in oven for 5 days and annealing at 120 °C in vacuum oven for 2 days.

**Broadband Dielectric Spectroscopy (BDS)**

Isothermal dielectric spectra were collected using a Novocontrol GmbH Concept 40 Broadband Dielectric Spectrometer over the frequency (\( f \)) range of 0.01 Hz - 3 MHz and over the temperature range of -110 to 220 °C. Temperature stability was controlled to within ±0.2 °C. Sample films that were 0.08 – 0.20 mm thick were prepared in the same way as the films used in the DMA experiments. The film samples were dehumidified in a Humidity Control Chamber (Model 503-20, Electro-tech Systems, Inc.) with relative humidity < 0.5% at room temperature for more than one week to decrease the influence of water on dielectric response. Sample discs of 2 cm diameter that were covered with
two very clean aluminum sheets on both sides were sandwiched between two gold-coated copper electrodes of 2 cm diameter and transferred to the instrument for data collection.

Data Analysis

Relaxation information was extracted by fitting the following Havriliak-Negami (HN) equation, to which is added a correction for dc conductivity, to experimental dielectric permittivity data:\(^7\)

\[
\varepsilon^*(\omega) = \varepsilon' (\omega) - i \varepsilon'' (\omega) = -i \left( \frac{\sigma_0}{\varepsilon_0 \omega} \right)^N + \sum_k \left[ \frac{\Delta \varepsilon_k}{1 + (i \omega \tau_{HN})^\alpha} \right]^{\beta} + \varepsilon_\infty
\]

(1)

\(\varepsilon^*\) is the complex permittivity for which \(\varepsilon'\) and \(\varepsilon''\) are the real and imaginary parts, respectively. \(\omega = 2 \pi f\), \(k\) is the number of relaxation peaks curves used in the curve fitting process. \(\Delta \varepsilon_k = (\varepsilon_s - \varepsilon_\infty)_k\) is the relaxation strength for a relaxation indexed by \(k\), where \(\varepsilon_s\) and \(\varepsilon_\infty\) are the real permittivities at limiting low and high frequency, respectively. \(\tau_{HN}\) is the Havriliak-Negami relaxation time. \(\alpha\) and \(\beta\) are parameters that quantify the breadth and asymmetry, respectively, of a given relaxation peak. \(\sigma_0\) is the dc conductivity due to either inherent charge carriers or impurities. The exponent \(N\) characterizes the nature of the charge hopping process as will be explained later. The actual relaxation time, or characteristic time scale over which molecular motions occur, is \(\tau_{max} = 1/(2 \pi f_{max}^2)\), where \(f_{max}\) is the frequency at the maximum in \(\varepsilon''\), is calculated using the equation:\(^8\)

\[
\tau_{max} = \tau_{HN} \left[ \sin \left( \frac{\pi \alpha \beta}{2 (\beta + 1)} \right) / \sin \left( \frac{\pi \alpha}{2 (\beta + 1)} \right) \right]^{1/\alpha}
\]

(2)

There are as many terms in the sum in equation 1 as there are observed relaxations. Spectra are curve-resolved into component peaks in the usual non-linear least-squares fashion.
The Ohmic conductivity - adjusted Kramers-Kröning (K-K) equation, shown below, is an integral transformation from the real to the imaginary permittivity evaluated at a frequency $\omega_0$:

$$
\varepsilon''(\omega_0) = \frac{\sigma_0}{\varepsilon_v \omega_0} + \frac{2}{\pi} \int_0^{\infty} \frac{\varepsilon'(\omega)}{\omega^2 - \omega_0^2} \, d\omega = \frac{\sigma_0}{\varepsilon_v \omega_0} + \varepsilon''_{kk}
$$

(3)

$\varepsilon_v$ is the vacuum permittivity. As in the H-N equation, measured values of $\varepsilon''(\omega_0)$ include resistive losses. The relaxations in the H-N equation emerge or become more clear after subtraction of the obscuring dc conduction term from measured values of $\varepsilon''(\omega)$ over the frequency range. However, equation 3 offers a route whereby this subtraction is not necessary because $\varepsilon''_{kk}$ only involves the real permittivity that, in principal, does not involve resistive loss. Pure relaxations can be extracted from experimental $\varepsilon'(\omega)$ values over a broad frequency range by performing the numerical integration of Steeman and van Turnhout that yields $\varepsilon''_{kk}$ vs. frequency. We have used this technique in the work reported here; the reader is directed to the details in their publication.9,10

Results and Discussion

DMA

Both SEBS and sSEBS samples exhibit two glass transitions that are greatly separated in temperature ($T$), as seen in the $E'$ and tan $\delta$ vs. temperature curves at 1 Hz in Figures IV-1 and IV-2, respectively. These results are in accordance with our earlier DMA studies of very similar materials.3,6

The rubbery plateau seen in Figure IV-1 does not greatly change for SEBS, 7.6% and 9.3% sulfonated SEBS as the curve segments are practically superimposed. However, for 11.7 and 14.1% sulfonation the plateau modulus drops and in this order. It
is unclear as to why $E'$ drops as it might be imagined that sulfonic acid groups would enhance the rubbery modulus through hydrogen bonding interactions. Perhaps, at these concentration levels, $\text{SO}_3\text{H}$ groups act as packing defects that disrupt cohesion in the hard domains. $E'$ for unsulfonated SEBS drops off at the end of the rubbery region while the curves for the sulfonated samples either hold constant or rise in some cases. Sulfonic acid groups might pose impediments to flow through hydrogen bonding interactions.

**Figure IV-1.** $E'$ vs. $T$ for SEBS and sSEBS samples with different percent sulfonation.

Figure IV-2 consists of the corresponding tan $\delta$ vs. $T$ curves for these samples. The lowest temperature transition peak at around -40 to -44 °C arises from segmental motions in the EB block phase. The high temperature transition at around 98 to 110 °C corresponds to the onset of long range block motions in the S block phase. The presence of two distinct glass transitions at temperatures approximately where they would be for the respective homopolymers is a signature of phase separation, here at the nanoscale.
Figure IV-2. Tan δ vs. T (°C) of SEBS and sSEBS samples with different percent sulfsulfonation.

For all sulfonation levels, $T_g$ (peak temperature) of the EB block domain is practically the same and approximately equal to that for unsulfonated SEBS. Thus, sulfonation of the PS blocks does not appear to influence macromolecular motions in the EB block domains, as seen by this method, although the BDS results, seen below, will show more sensitivity. On the other hand, $T_g$ of the styrene block domains in sSEBS shifts to higher temperatures relative to unsulfonated SEBS and increases with increasing percent sulfonation. This is envisioned as being due to restriction of S block segmental motions by hydrogen bonded SO$_3$H groups. These restrictions may also be responsible for the increasing suppression of the tan δ peak for this transition. A third transition above the styrene block glass transition appears on each sSEBS curve as well as on the unsulfonated SEBS curve and shifts to higher temperature with increased sulfonation. As discussed earlier, this third transition may arise from SO$_3$H aggregate sub-domains within
the styrene block domains. With regard to SEBS, the nature of the third transition is different and might be due to a domain disruption as described by Tse.

**Dielectric Spectroscopy**

All samples were measured at temperatures lower than the order-disorder transition temperature (T_{od}) for these materials as previously reported (~240 °C). A typical 3-dimensional ε'' vs. f and T response surface for a sulfonated sample is displayed in Figure IV-3. As mentioned, a signature of phase separation in block copolymers is two distinct glass transitions in dielectric spectra that are close to the T_g values of the corresponding homopolymers which is seen to be the case for the BDS as well as the DMA results. Thus, SEBS seems to retain a two-phase nature at the sulfonation level of 11.7% as there are two well separated peaks seen as two ridges on the two dimensional surface in Figure 3. The ridge at lower temperatures is due to segmental relaxation in the EB block domains and the ridge at higher temperature is assigned to segmental relaxation in the S block domains. High ε'' values at low f and high T are attributed to dc conduction as represented by the first term in equation 1. All other sSEBS samples as well as unmodified SEBS exhibit two similar peaks that are associated with EB and S block domains.
**Figure IV-3.** ε″-f–T response surface for sSEBS with 11.7% sulfonation.

ε″ vs. T plots at various frequencies for unsulfonated SEBS are displayed in Figure IV-4. In accordance with the DMA results in Figure IV-2, the relaxations labeled \( \alpha_{EB} \) and \( \alpha_{PS} \) are clearly the glass transitions of the EB and S block phases. The peak, labeled \( \beta \), below the temperature of the \( \alpha_{EB} \) transition, must be due to very local motions in the totally glassy copolymer. The authors are not aware of a transition at this temperature obtained using dielectric spectroscopy in either sulfonated or unsulfonated polystyrene (PS) although studies of the \( \alpha \) transition for this polymer have been well-discussed.\(^{13}\) Three weak sub-\( T_g \) relaxations were observed in dynamic mechanical studies of PS and lightly crosslinked PS.\(^{14}\) Of these relaxations, one is in the vicinity of the \( \beta \)
relaxation for SEBS seen in Figure IV-4 and this relaxation was suggested to be associated with infrequent head-to-head polymerization of styrene monomers. Atornjitjawat et al. identified a sub-$T_g$ peak in sulfonated PS that was proposed to arise from local motions of sulfonated phenyl groups in the glassy state.$^{15,16}$ Of course, since this relaxation occurs below the glass transition of the inner block domains it could also be due to short range motions in the EB regions, thereby complicating an assignment of origin.

**Figure IV-4.** $\varepsilon''$ vs. T for unsulfonated SEBS at the three indicated frequencies.

There is a relaxation, labeled $\alpha'$, between $\alpha_{\text{EB}}$ and $\alpha_{\text{PS}}$. Only speculation can be offered as to the origin of this relaxation. One concept involves molecular motions that are confined to distinct mixed S-EB interphase regions of significant thicknesses. Interfacial thickness, based on AFM tapping mode/phase sectional analysis, has been
estimated to be around 10-20 nm for SEBS having the same block composition.\textsuperscript{17} Another suggestion for this peak involves interfaces, but due to a hard domain/soft domain interfacial polarization relaxation that arises from the gradient of dielectric permittivity across the phase boundaries.

It is suggested that the relaxation at the highest temperatures beyond the $\alpha_{PS}$ relaxation, that becomes more distinct with decrease in frequency, is due to polymer/electrode interfacial polarization, labeled $\alpha_{EP}$. This phenomenon was seen in dielectric loss spectra for 7% sulfonated polystyrene by Atorngitjawat et al.\textsuperscript{15} The low $f$-high $T$ phenomenon arises from the alternating accumulation and dissipation of alternating charge near the blocking electrodes. This suggestion is supported by a high low frequency limiting value of $\varepsilon'$ as seen later in this report (Figure 9). All transitions in Figure IV-4 shift to higher $T$ with increase in frequency owing to an increasing inability of the relaxing elements to execute their motions within the half period of the applied voltage.

$\varepsilon''$ vs. $T$ plots at various frequencies for sSEBS (14.1\%) are displayed in Figure IV-5. The $\alpha_{EB}$ and $\alpha_{PS}$ relaxations are the glass transitions of the EB block and S block phases in line with the interpretation of the DMA results for sSEBS (14.1\%) in Figure IV-2. Similar to the interpretation for unsulfonated SEBS, the low temperature $\beta$ relaxation is assigned to local motions in either EB or S block phases. Unlike unsulfonated SEBS, the peak suggested to be related to interphase regions or interfacial polarization relaxation is not seen between the two glass transitions in sSEBS (14.1\%). Sulfonated PS blocks would not be expected to mix with EB blocks, even sparingly, owing to the increase in polarity contrast between the blocks.
Figure IV-5. $\varepsilon''$ vs. $T$ for sSEBS(14.1%) at four indicated frequencies.

There are essentially two features in the higher temperature range. The $\alpha_{PS}$ relaxation peak shifts to lower temperatures with decrease in frequency such that at the two lowest frequencies it becomes buried in another peak ($\alpha_{EP}$) that becomes stronger with decreasing frequency. The reason for the rightward shift of $\alpha_{PS}$ with increasing frequency is that higher temperatures are required to bring the range of the relaxation time scale down to the time scale of the experiment, i.e., the half period of electric field oscillation = $(2f)^{-1}$. The final large rise in $\varepsilon''$ with increase in temperature may be due to sample | electrode interfacial polarization because the curves rise to very high $\varepsilon''$ values with decreasing frequency. To be sure, especially because this sample contains strong acid groups, dc conductivity might be superimposed on this strong feature, but the fact
that the plots ultimately curve downward supports the idea of a sample electrode interfacial polarization relaxation.

The effect of sulfonation on relaxations is seen in the $\varepsilon''$ vs. $T$ plots for 13.81 kHz in Figure IV-6.

![Figure IV-6. $\varepsilon''$ vs. $T$ for SEBS and various sSEBS at $f = 13.81$ kHz.](image_url)

The $\alpha_{PS}$ relaxation for all sulfonated samples appears at higher temperatures than for unsulfonated SEBS, shifting to progressively higher temperatures with increased degree of sulfonation. This is viewed, again, as being due to the increasing restrictions on S block motions posed by hydrogen bonding between increasingly more SO$_3$H groups that might form a sub-phase at higher sulfonation degrees, as discussed earlier. The monotonic upward vertical curve displacement is attributed to the fact of increasingly greater dipole moment per unit volume. The largest vertical displacement is between the
curves for unsulfonated SEBS and the first in the sulfonation series (7.6%). The $\alpha_{EB}$ relaxation in sSEBS is in higher temperature than that of the EB block domain in unsulfonated SEBS. While there are no $SO_3H$ groups in the inner blocks, this behavior, in speculation, may be due to some form of inter-phase coupling.

**Segmental Relaxation Process**

Relaxation times ($\tau_{max}$) associated with the S and EB block domain glass transitions were determined from fits of the HN equation to experimental data in the appropriate frequency regions at different temperatures and the results are seen in Figures IV-7 and IV-8. For both relaxations the $\log_{10} \tau_{max}$ vs. $1/T$ curves are nonlinear and exhibit upward curvature.

*Figure IV-7.* $\log_{10} \tau_{max}$ vs. inverse temperature for the S block domain relaxation in SEBS and sulfonated SEBS samples of indicated percent sulfonation.
This nonlinearity is often represented by the Vögel-Fülcher-Tammann (VFT) equation with three empirical parameters: \(^{18}\)

\[
\tau(T) = \tau_0 \exp \left( \frac{B}{T - T_0} \right)
\]  

(4)

\(\tau_0\) is a hypothetical relaxation time at infinite temperature, \(B\) is a fitting parameter related to polymer ‘fragility’, \(^{19}\) and \(T_0\) is the Vögel temperature at which segmental motions are frozen upon quasi-static cooling. All best-fit parameters in this empirical equation are listed in Tables IV-1 and IV-2 for the S and EB block domain relaxations, respectively.

**Table IV-1.** VFT Equation Best-fit Parameters and Fragility \((F)\) for the S block Phase Glass Transition for SEBS and sSEBS Variants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (K)(^{a})</th>
<th>(\log_{10} \tau_0) (s)</th>
<th>(B) (deg K)</th>
<th>(T_0) (K)</th>
<th>(T_{ref}) (K)</th>
<th>(F)(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>370</td>
<td>-12.3</td>
<td>1286</td>
<td>313</td>
<td>359</td>
<td>97</td>
</tr>
<tr>
<td>sSEBS(7.6%)</td>
<td>369</td>
<td>-14.9</td>
<td>2143</td>
<td>301</td>
<td>363</td>
<td>87</td>
</tr>
<tr>
<td>sSEBS(9.3%)</td>
<td>370</td>
<td>-12.7</td>
<td>1622</td>
<td>312</td>
<td>367</td>
<td>84</td>
</tr>
<tr>
<td>sSEBS(11.7%)</td>
<td>374</td>
<td>-13.6</td>
<td>2360</td>
<td>295</td>
<td>370</td>
<td>67</td>
</tr>
<tr>
<td>sSEBS(14.1%)</td>
<td>379</td>
<td>-10.7</td>
<td>1171</td>
<td>339</td>
<td>387</td>
<td>87</td>
</tr>
</tbody>
</table>

\(^{a}\)\(T_g\) values are from the DMA \(\tan \delta\ vs. T\) plot. \(^{b}\)Fragility was calculated using equation 4.

**Table IV-2.** VFT Equation Best-fit Parameters and Fragility \((F)\) for the EB Block Phase Glass Transition for SEBS and sSEBS Variants.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g) (K)(^{a})</th>
<th>(\log_{10} \tau_0) (s)</th>
<th>(B) (K)</th>
<th>(T_0) (K)</th>
<th>(T_{ref}) (K)</th>
<th>(F)(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>229</td>
<td>-7.9</td>
<td>529</td>
<td>188</td>
<td>217</td>
<td>59</td>
</tr>
<tr>
<td>sSEBS(7.6%)</td>
<td>230</td>
<td>-11.4</td>
<td>1638</td>
<td>162</td>
<td>224</td>
<td>41</td>
</tr>
<tr>
<td>sSEBS(9.3%)</td>
<td>230</td>
<td>-10.8</td>
<td>1323</td>
<td>173</td>
<td>226</td>
<td>46</td>
</tr>
<tr>
<td>sSEBS(11.7%)</td>
<td>230</td>
<td>-8.7</td>
<td>830</td>
<td>184</td>
<td>225</td>
<td>47</td>
</tr>
<tr>
<td>sSEBS(14.1%)</td>
<td>231</td>
<td>-9.9</td>
<td>1195</td>
<td>172</td>
<td>224</td>
<td>42</td>
</tr>
</tbody>
</table>

\(^{a}\)\(T_g\) values are from DMA \(\tan \delta\ vs. T\) plot. \(^{b}\)Fragility was calculated using equation 4.
There is no distinctive trend in the VFT parameters for the S block phase with increase in sulfonation. A hidden variable that may cause this non-monotonic behavior is a morphology shift that depends on degree of sulfonation as seen in the microscopic studies of sSEBS mentioned earlier. The same can be said for the EB phase VFT parameters.

In Figure IV-7, save for the crossover of the closely separated curves for SEBS and sSEBS (7.6%), the S block domain relaxation time monotonically increases with increased degree of sulfonation at a given temperature. As mentioned, this slowing of chain dynamics is viewed as being due to restrictions on S block mobility posed by hydrogen bonds between SO$_3$H groups.

Figure IV-8. Log$_{10}$ $\tau_{\text{max}}$ vs. inverse temperature for the EB block domain relaxation in SEBS and sulfonated SEBS samples of indicated percent sulfonation.
Figure IV-8 shows that relaxation times for the EB block phase in the sulfonated samples are less sensitive to percent sulfonation as compared to the relaxation times of the S block phase. Moreover, they are longer than that for unsulfonated SEBS at lower temperatures where the curves merge with increasing temperature. It was seen in Figure IV-2 that the glass transition of the EB block domain is approximately unaffected in the DMA curves. This comparison demonstrates how dielectric spectroscopy analysis is more sensitive than dynamic mechanical analysis to changes in polymer chemical structure and coupling between relaxations.

Polar groups may have been created in the EB blocks during sulfonation at rare residual C=C double bonds that may have survived SEBS hydrogenation, although this would have to be verified by spectroscopic means. An increased polarity of the EB blocks will shift this relaxation. Also, the increase in relaxation time may be affected by morphological differences generated by sulfonation as seen in our earlier studies. In Figure IV-8, all degrees of sulfonation result in similar relaxation times, which might support the first hypothesis.

The quantity ‘fragility’, $F$, viewed as an index of cooperative motions in polymers as influenced by intermolecular interactions, is defined as

$$F = \frac{d \log(\tau_{\text{max}})}{d(T_{\text{ref}} / T)} \bigg|_{T=T_{\text{ref}}} = \frac{B / T_{\text{ref}}}{(\ln 10)(1 - T_0 / T_{\text{ref}})^2}$$

(5)

$T_{\text{ref}}$ is a reference temperature calculated using the VFT equation when the segmental relaxation time is 1 sec. $F$ is a measure of the sensitivity with which $\tau_{\text{max}}$ responds to change in temperature and is correlated with the degree of intermolecular coupling. As intermolecular interactions become stronger the material becomes more fragile because intermolecular coupling and the relaxation time diminish more rapidly with
increasing temperature.\textsuperscript{26} For a hydrogen bonded system, intermolecular interactions are significantly greater than $kT$ so that it is possible that intermolecular hydrogen bonds would restrict chain motions and thus render the system more fragile.

As seen in Table IV-1, $F$ for the S block in unsulfonated SEBS is 97, similar to a reported value for pure PS ($F = 101$)\textsuperscript{19}, although Atorngitjawat et al. cited a lower value ($F = 78$) for pure PS.\textsuperscript{15} Also seen in Table IV-1 is that $F$ for all samples having sulfonated PS blocks is smaller than values for unsulfonated blocks in SEBS which seems counterintuitive. It has been reported that incorporation of hydrogen bonds within styrene containing polymers does not show a pronounced impact on fragility.\textsuperscript{15,22}

One explanation is that hydrogen bonding may hinder macromolecular rearrangement so as to diminish phase separation, leading to less fragile behavior.\textsuperscript{27,28} $F$ for the S block glass transition steadily decreases with increase in sulfonation, with the 14.1\% variant being the exception. The fact that the fragility of the EB block domain (59) is lower than that of the PS block domain in unsulfonated SEBS is reasonable. The fragility of the EB block phase shows a similar relationship between sSEBS and SEBS in that $F$ for the latter is the largest. These results of fragility for SEBS and sSEBS might be related to a morphological variance for these samples. A TEM study of SEBS and sSEBS by Blackwell et al. showed that SEBS exhibits hexagonal-packed PS cylinders, sSEBS with 8\% sulfonation shows frustrated microphase separation, and sSEBS with 14\% sulfonation degree has lamellar morphology.\textsuperscript{4} This morphological change suggests that polar acid groups affect the rearrangement of polymer chains. sSEBS(11.7\%) might be a transitional morphology. When sulfonation increases to 14.1\%, the intermolecular coupling may increase again, which might be the reason why the S block fragility of
sSEBS(14.1%) is higher than that of the counterpart of sSEBS(11.7%). The decrease in fragility in the EB block domains with sulfonation might occur because the sulfonated S domains restrict the arrangement of EB blocks.

**Dielectric Loss Permittivity via Kramers-Kröning Integral Transform**

As mentioned, dielectric loss spectra of polymers that incorporate intended or impurity charge carriers can show high dc conductivity at low $f$ and high $T$ which can obscure relaxation peaks.\textsuperscript{23,29,30} $\varepsilon''_{kk}$ in equation 3 does not involve this contribution because it is derived from the real permittivity that does not involve dc conduction.\textsuperscript{9,10,16} $\varepsilon''_{kk}$ of our SEBS and sSEBS samples were calculated from $\varepsilon'$ data as mentioned earlier to uncover relaxations that are obscured by the dc contribution.

*Figure IV-9.* $\varepsilon''$ and $\varepsilon''_{kk}$ vs. $f$ for unsulfonated SEBS at 190 °C with indicated regions of polymer/electrode interfacial polarization ($\alpha_{EP}$), suggested internal interfacial polarization ($\alpha_{MWS}$) relaxations and S block phase segmental relaxation ($\alpha$).
\( \varepsilon''_{kk} \) vs. \( f \) curves for unsulfonated SEBS at 190 °C in Figure IV-9 indicate three processes. Also plotted in Figure IV-9 is the corresponding \( \varepsilon'' \) vs. \( f \) curve on which dc conduction is quite evident despite the fact that there are no intentional (but impurity) charge carriers in the unsulfonated block copolymer. The linear dc-related curve section on this curve is indeed not present on the \( \varepsilon''_{kk} \) curve. The relaxation labeled \( \alpha_{\text{MWS}} \) (MWS = Maxwell–Wagner–Sillars) is tentatively assigned to relaxation of polarization at the boundaries of the S and EB block domains. The \( \alpha_{\text{EP}} \) relaxation is attributed to accumulation \( \leftrightarrow \) dissipation of charge at the sample/electrode interface, as before.\(^{31}\)

\[ \text{Figure IV-10. } \varepsilon' \text{ vs. } f \text{ of unsulfonated SEBS at 190 °C.} \]

dc conduction can contribute significantly to dielectric loss spectra at low \( f \) when \( T > T_g \) because long range segmental mobility can facilitate charge hopping.\(^{32}\) In Figure IV-9, there is large dc conductivity over a broad range of \( f \) because the temperature of
190 °C considerably exceeds $T_g$ of the S block domains. The data suggests that the conductivity arises from charges in the S block domains that are liberated above $T_g$. The $\alpha_{\text{MWS}}$ peak may arise from the accumulation $\leftrightarrow$ dissipation of impurity ions at S/EB interfaces as well as to differences in the dielectric permittivities of these phases, although this is offered in speculation. The high permittivity values seen in the corresponding $\varepsilon'$ vs. $f$ graph for 190 °C in Figure IV-10 strongly suggests sample/electrode polarization, at least at the lowest frequencies.

![Figure IV-11](image.png)

*Figure IV-11.* $\log_{10} \varepsilon''_{kk}$ vs. $\log_{10} f$ for unsulfonated SEBS at three high temperatures showing suggested regions of electrode polarization relaxation ($\alpha_{\text{EP}}$) and MWS internal interfacial relaxation ($\alpha_{\text{MWS}}$) in addition to the S block segmental relaxation ($\alpha$) process that is partly off-scale at high $f$.

Figure IV-11 shows $\log_{10} \varepsilon''_{kk}$ vs. $\log_{10} f$ curves for unsulfonated SEBS at temperatures of 170, 190 and 220 °C. The curves are vertically displaced upward while the peaks shift to higher $f$ with increasing $T$ indicating shorter relaxation times. The $\alpha$
peak is off-scale to the right; only the low frequency wing is visible. Figure IV-12 shows log τ vs. 1/T for the suggested MWS relaxation peak. The curve shape suggests VFT-like behavior which is compatible with results in some reports of MWS polarization in polymers in which the charge motion is said to be coupled to long range segmental motions. For the case at hand, these motions would involve both EB and S blocks as the curves were obtained at temperatures above the S block phase \( T_g \). In this condition, there would still be phase separation as the temperatures are beneath an order-disorder transition, but both block domains would be in a liquid-like state. As there would be segmental mobility on both sides of S/EB interfaces, it is reasonable that an interfacial polarization relaxation would be coupled to these motions. The VFT parameters were calculated to be \( \tau_0 = 10^{-5.75} \text{s} \), \( T_0 = 335 \text{ K} \) and \( B = 1022 \text{ K} \).

![Graph](image-url)

**Figure IV-12.** Inverse temperature dependence of log \( \tau_{\text{max}} \) for the suggested MWS relaxation for unsulfonated SEBS.
The log $\varepsilon''$ vs. log $f$ curve for 14.1% sulfonated SEBS seen in Figure IV-13 exhibits considerable dc conduction as given evidence by the straight line section of the curve at low $f$. This feature is not present on the corresponding $\varepsilon''_{kk}$ curve in this figure, on which two additional relaxations appear in addition to that for segmental relaxation which is partially off-scale. This example illustrates the benefit of using the Kramers-Krönig transformation to uncover relaxations hidden by an overwhelming dc contribution in the low $f$ regime. These relaxations are tentatively assigned to, in order of increasing $f$, polymer/electrode polarization ($\alpha_{EP}$), MWS relaxation ($\alpha_{MWS}$) and segmental relaxation in the S block domains.

*Figure IV-13.* $\varepsilon''$ and $\varepsilon''_{kk}$ vs. $f$ at 200 °C for 14.1% sulfonated SEBS.

The EP relaxation in sulfonated SEBS should involve mobile protons in the vicinity of the electrodes and their dissociation from sulfonic acid groups increases with increasing temperature to enhance this process.\(^{13}\)
This, in fact, is seen in Figure IV-14 for the EP relaxation where the curves in the low \( f \) regime rise with increase in temperature. This upswing is not due to dc conductivity, as this effect has been subtracted. The signature of EP relaxation is a peak\(^{33}\) and it is seen that the curves in fact turn down at the lowest frequencies in Figure IV-14. The sharp increase in \( \varepsilon' \) with decreasing \( f \) and elevation of the curves with increasing temperature seen in Figure IV-15 supports the assignment of the EP relaxation at low \( f \).

Also seen in Figure IV-14 is rightward shifting of relaxation peaks with increase in temperature. The MWS relaxation time for 14.1% sulfonated SEBS (14.1%) was extracted using the HN equation. \( \log \tau_{\text{max}} \) vs. \( 1/T \) for this process exhibits VFT behavior as seen in Figure IV-16. The best-fit VFT parameters are \( \tau_0 = 10^{-4.87} \) s, \( T_0 = 370 \) K and \( B = 479 \) K. This value of \( B \) is considerably smaller than that for unsulfonated SEBS (1022 K). The VFT parameters, within the context of relaxation of polarization at interfaces,
Figure IV-15. \( \varepsilon' \) vs. \( f \) for sSEBS(14.1%) at indicated temperatures.

Figure IV-16. Inverse temperature dependence of \( \log \tau_{\text{max}} \) for the MWS relaxation for sSEBS (14.1%).
would be controlled by the ability of charges to accumulate at phase boundaries as facilitated by segmental motions. MWS polarization relaxation in sulfonated SEBS might also involve differences in the mobility of protons in SO$_3$H rich S block phase subdomains and in their mobility in unsulfonated regions.

Charge Conduction

Impurity charges in polymers, even in concentrations of tens-of-ppm, can give rise to observable dc conductivity in dielectric loss spectra of polymers.$^{34,35}$ dc conduction associated with mobile ions in polymers above $T_g$ is coupled to long range chain motions that become faster with increasing temperature. Clearly, the charge conductors in sSEBS are protons donated by strong acid groups in the outer blocks while unknown impurity charges must account for the conductivity of unsulfonated SEBS. Not only are the nature and concentration of impurity charges unknown, but are not expected to be reproducible from sample-to-sample so that caution should be observed in comparing the conductivity of SEBS with sSEBS materials. Nonetheless, studies of unsulfonated SEBS studies were performed to provide baseline data.

Dielectric spectra of SEBS and sSEBS show dc conduction at temperatures above the glass transitions in the styrene and sulfonated styrene block phases, but not significant conduction between the temperature range spanning the EB block phase $T_g$ and the styrene (or sulfonated styrene) block phase $T_g$. This is taken to indicate that the charges in either case mainly reside in the hard block phases which have to be rendered liquid-like for long range charge hopping to occur.

$\sigma_0$ was extracted from the fit of equation 1 to permittivity data at different temperatures and is plotted vs. 1000/$T$ for SEBS and sSEBS in Figure IV-17. The curve
for unsulfonated SEBS samples is different than those for the sulfonated samples – the latter being similar to each other - in that conductivity is less sensitive to temperature. All curves are nonlinear and display VFT-like behavior.

![Graph showing conductivity vs. inverse temperature](image)

**Figure IV-17.** $\sigma_0$ vs. inverse temperature for SEBS and sSEBS for indicated percent sulfonation for temperatures above $T_g$ for the PS block domains.

Conductivity, in general, can be written as $\sigma = \rho \mu$ where $\rho$ is the charge carrier density and $\mu$ is charge mobility. $\rho$ would increase with increase in percent sulfonation (proton concentration) and this would account for the monotonically upward shift in the curves in Figure IV-17. $\mu$, of course, would not be expected to be the same for each sulfonated modification but would increase with increased percent sulfonation because the average elemental proton hopping distance, i.e., distance between SO$_3$H groups, would decrease. The case of sSEBS(7.6%) and sSEBS(9.3%) samples may be exceptional, although they show similar $\sigma_0$ and the curves merge at the lowest
temperatures. It is concluded that the increase of ionic conductivity with increasing temperature is due to higher mobility of polymer chain segments as well as more activated protons, as well as the coupling of these processes.

Unsulfonated SEBS shows higher $\sigma_0$ values than sSEBS below some temperature as the SEBS curve intersects the sSEBS(11.7%) curve at around 410 K. While the nature of impurity charges in these unsulfonated SEBS samples is unknown, the sulfonated PS block phase in sSEBS has a higher $T_g$ than unsulfonated SEBS so that the chain sections in these blocks require a higher temperature to activate and facilitate charge hopping.

The temperature dependence of conductivity in polymers above their glass transition temperature often obeys the following VFT-like equation:\textsuperscript{23,33,34,36}

$$\sigma_0(T) = \frac{A}{\sqrt{T}} \exp\left(\frac{B'}{T - T'_0}\right)$$  \hspace{1cm} (6)

$A$, $B'$, and $T'_0$ are empirical parameters obtained by fitting equation 6 to experimental conductivity vs. $T$ data. Equation 6 was seen to fit well to the data for both SEBS and sSEBS. The VFT-like behavior of the experimental $\sigma_0$ vs. $T$ data implies that this conduction process is coupled to polymer chain segmental motions as discussed earlier. The fitted values of $A$, $B'$, and $T'_0$ are listed in Table IV-3. $T'_0$ is considerably lower than $T_0$ in equation 4 for the PS block segmental relaxation. While these two temperatures might be related, they are not necessarily the same. While $T_0$ is viewed as a hypothetical upper bound temperature at which segmental motions are frozen during quasi-static cooling, $T'_0$ might be considered as a temperature beneath which long range charge migration essentially ceases. Given the validity of this interpretation, it would seem that
conductivity shuts down before the free volume in the PS block domains becomes small to the degree of preventing segmental motion.

Table IV-3. VFT-like Conductivity Equation Best-fit Parameters for SEBS and sSEBS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\log_{10} A$ (K$^{1/2}$/S/cm)</th>
<th>B′ (K)</th>
<th>T₀′ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>-9.3</td>
<td>923</td>
<td>292</td>
</tr>
<tr>
<td>sSEBS(7.6%)</td>
<td>-8.4</td>
<td>1317</td>
<td>305</td>
</tr>
<tr>
<td>sSEBS(9.3%)</td>
<td>-6.7</td>
<td>2050</td>
<td>282</td>
</tr>
<tr>
<td>sSEBS(11.7%)</td>
<td>-4.8</td>
<td>2766</td>
<td>261</td>
</tr>
<tr>
<td>sSEBS(14.1%)</td>
<td>-3.9</td>
<td>2790</td>
<td>267</td>
</tr>
</tbody>
</table>

The quantity A, to which conductivity is directly proportional, increases with increasing degree of sulfonation, which is reasonable. B′, having units of temperature, monotonically increases with increase in percent sulfonation. Given the fact that the curves in Figure IV-17 are nonlinear, B′ cannot be interpreted in terms of activation energy, but rather must be related to cooperative segmental motions above a glass transition.

Correlation between Segmental Relaxation and Ionic Conductivity

In glass-forming liquids dc conduction arises from the motion of charges undergoing translational hopping that is coupled to cooperative motions in the medium. This coupling is embodied in the Debye-Stokes-Einstein (DSE) relationship:

$$\sigma \tau \equiv \text{constant} \quad (7)$$

$\sigma$ is the dc conductivity and $\tau$ is the relaxation time. Shorter relaxation times (faster chain motions) correspond to greater conductivity. This equation holds for ordinary liquids and many simple glass-forming fluids in the super-cooled regime, including
When equation 7 is not obeyed, polymers may follow the phenomenological fractional Debye-Stokes-Einstein (FDSE) equation:

$$\sigma \tau^s \equiv \text{constant} \quad (8)$$

where the exponent, $s$, is less than one.

The breakdown of the DSE relation has been explained in a number of ways. One explanation involves dynamic heterogeneity in the form of spatially correlated regions of high/low mobility. Within the context of SEBS, one can think of two chemically distinct hard and soft block domains that are covalently coupled.

Somewhat related is the concept of microstructural heterogeneity on a smaller scale - perhaps a broad free volume distribution - manifested by a stretched exponential relaxation in the time domain. While relaxation time and conductivity are coupled, the critical free volume required for small charge motions would be less than for the cooperative motions of a string of chain segments.

dc conductivity vs. S block domain $\alpha$ relaxation time curves for SEBS and the sSEBS samples are co-plotted in log-log fashion in Figure IV-18. The plots are quite linear for all samples so that the FDSE equation is obeyed and the best-fit parameters are listed in Table IV-4. There is a monotonic elevation of the graphs with increasing percent sulfonation which is a reflection of increases in charge carrier density, $\rho$. Taken from the slope, $s$ for unsulfonated SEBS is 0.43. Values of $s$ for all sSEBS samples are higher and in the narrow range of 0.6 - 0.7. The large difference in $s$ values for SEBS and sSEBS might indicate different nature in the charge conductors and the effect of sulfonation on the glass transition.
Figure IV-18. Correlation between $\sigma_0$ and $\tau_{\text{max}}$ for the PS block domain $\alpha$ relaxation for SEBS and sSEBS samples.

Table IV-4. FDSE Equation Best-fit Parameters for SEBS and sSEBS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope (-s)</th>
<th>Intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBS</td>
<td>-0.43</td>
<td>-15.1</td>
</tr>
<tr>
<td>sSEBS(7.6%)</td>
<td>-0.64</td>
<td>-15.7</td>
</tr>
<tr>
<td>sSEBS(9.3%)</td>
<td>-0.70</td>
<td>-17.0</td>
</tr>
<tr>
<td>sSEBS(11.7%)</td>
<td>-0.69</td>
<td>-17.5</td>
</tr>
<tr>
<td>sSEBS(14.1%)</td>
<td>-0.62</td>
<td>-14.4</td>
</tr>
</tbody>
</table>

Conclusions

Macromolecular dynamics in SEBS and sSEBS triblock copolymers were studied by broadband dielectric spectroscopy and complemented by dynamic mechanical analysis. Relaxations corresponding to the EB and S block phases were identified and
the temperature dependence of relaxation time in both cases was VFT-like, which is characteristic of long range segmental behavior above the glass transition. The S block phase glass transition in sSEBS shifts to higher temperatures with increased sulfonation, which is rationalized in terms of restrictions on S block mobility posed by hydrogen bonds between SO$_3$H groups. From a DMA perspective, $T_g$ for the EB block domains is essentially unchanged with sulfonation, but is seen to shift somewhat upward using the more sensitive method of BDS. A relaxation at temperatures lower than the EB block domain glass transition appears in spectra for both SEBS and sSEBS is suggested to be due to local chain motions. In SEBS and sSEBS the signature of sample/electrode interfacial polarization was present. A loss peak at temperatures above the S block phase glass transition for both SEBS and sSEBS is speculated to arise from oscillating polarization at interfaces between liquid-like S and liquid-like EB block phases. The relaxation time vs. temperature behavior for this interfacial polarization was VFT-like which is logical since long range segmental motions are active on both sides of the interfaces.

The Kramers-Kröning integral transformation was used to calculate conductivity-free loss permittivity spectra from real permittivity spectra so that relaxations can be viewed unobscured. The temperature dependence of the dc conductivity for both SEBS and sSEBS polymers also obeys a VFT-like behavior which implies that the motion of charges is coupled to segmental motions. Finally, the relationship between the dc conductivity and segmental relaxation time obey the fractional Debye-Stokes-Einstein equation for both SEBS and sSEBS polymers.
In summary, relaxations in unsulfonated and sulfonated SEBS block copolymers have been identified and placed on a quantitative level and correlated with the transport of protons through these media in these particular conditions. These studies demonstrate the potential of broadband dielectric spectroscopy in the exploration of the relationship between charge transport, macromolecular dynamics and morphology in membranes.

Acknowledgments

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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

sSEBS/SrTiO$_3$ nanocomposite films were successfully prepared via in situ sol-precipitation of precursors in sSEBS film templates, with SrTiO$_3$ content of 10-15 wt%. The crystalline SrTiO$_3$ nanoparticles were formed in sulfonated styrene block domains and nanoparticle morphology was controlled by the domain morphology. Introduction of SrTiO$_3$ in composite films showed enhancement of dielectric constant and shift of dielectric dissipation factor.

sSEBS/silicate nanocomposite membranes exhibited improved mechanical properties with silicate incorporation. The proton conductivity of sSEBS/silicate membranes showed maxima at silicate content of 10 wt% for each series of composite samples. The morphology-property (methanol permeation and proton conductivity) relationship study addressed the influence of morphology on properties, which provided information for future development of novelty materials. The finding of maximum conductivity provided opportunity for future optimization with adjustment of material parameters.

Macromolecular dynamic of sSEBSs were investigated by BDS and complemented by DMA. The relaxation times of styrene and ethylene-co-butylene block phases were quantified and their temperature dependence obeyed VFT behavior. The temperature dependence of the dc conductivity for SEBS and sSEBS polymers follow a VFT-like behavior which implied that the motion of charges was coupled to segmental motions. These studies demonstrate BDS is an effective technique to explore dynamics of block copolymers.
Morphological characterization with TEM and AFM exhibited morphology of SrTiO$_3$ in rods cluster, selectively inserted in hydrophilic domains in sSEBS film templates. In current synthesis, the reaction system was heated for over 15 hours to drive crystallization of SrTiO$_3$ inside sSEBS film after hydrolysis of titanium complex and diffusion of strontium cations. During this reaction time, it is believed that SrTiO$_3$ rod clusters had already developed into some equilibrate morphology. To observe the evolution process of SrTiO$_3$ nanoparticle morphology (size and shape), the samples taken at different reaction time should be characterized with TEM. For example, the samples during preparation can be taken every hour for TEM observation.

For energy storage materials, high dielectric constant is desired in order to obtain high stored energy density. In terms of some prediction model, effective dielectric constant of polymer/inorganic composites (including sSEBS/SrTiO$_3$) will increase with inorganic volume ratio. In future studies, reaction parameters could be optimized to obtain high SrTiO$_3$ uptake.

Synthesis of sSEBS/BaTiO$_3$ is expected to be explored. In current research, Ba(Cl)$_2$ was used to replace Sr(NO$_3$)$_2$ in a typical preparation of sSEBS/SrTiO$_3$. The XRD pattern of sSEBS/BaTiO$_3$ film did not show diffraction peaks of crystalline BaTiO$_3$, suggesting crystalline BaTiO$_3$ particles were not formed inside sSEBS film. However, the white BaTiO$_3$ powders were prepared in the relevant liquid phase, and XRD pattern of BaTiO$_3$ powders indicated good crystalline structure. In literature, the synthesis of crystalline BaTiO$_3$ in liquid phase required higher temperature and longer time than those of SrTiO$_3$ synthesis. The faster diffusion rate of Sr cations and smaller atomic diameter
were proposed to be responsible for easier crystallization of SrTiO$_3$. To synthesize crystalline BaTiO$_3$ inside sSEBS, a suitable environment inside sSEBS template might be important. In the future studies, it is possible to obtain crystalline BaTiO$_3$ by adjusting reaction parameters.

To be used as energy storage materials, low dielectric loss is desired. Since energy storage materials are expected to work at high frequency range, the dielectric property at frequency > 100 kHz is critical. Our sSEBS/SrTiO$_3$ showed relatively high dielectric loss. This high dielectric loss might arise from various factors, such as acid groups, metal cations, dc conductivity, and interfacial polarization. Crosslinking of acid groups can consume acid groups and reduce the dielectric loss caused by acid groups. A simple crosslinking method of post-treatment of sulfonated fuel cell membranes can be explored for sSEBS/SrTiO$_3$. In this method reported in literature, a membrane was immersed into phosphorus pentoxide:methanesulfonic acid for 10 s and cured on a hot plate at 80 °C for 24 h under a nitrogen atmosphere.$^{1,2}$

In preparation of sSEBS/SrTiO$_3$ with sSEBS film as template, other block copolymers containing hydrophilic functional groups (i.e., COOH and OH) are suggested to be explored as templates. The living free radical polymerization can provide a wide variety of candidates for this type of polymers.

Study of sSEBS/Silicate Membranes

In our formulation for preparation of sSEBS/silicate membranes, the weight ratio of sSEBS and TEOS was in the range from ~3/1 to ~2/3. In comparison to literature, our loading of TEOS is much larger than other similar preparation with TEOS or in the high content range.$^3$ In our research, the silicate particle size increase with silicate content, and
the large silicate nanoparticles broadened hydrophilic domains, leading to high methanol permeability. The low loading of TEOS (weight ratio of sSEBS/TEOS in 1/9 – 3/1) is suggested to explore for future preparation of sSEBS/silicate. The low loading of TEOS is possible to reduce silicate particle size and relevant hydrophilic domains, which provides opportunity in obtaining good balance in properties such as methanol permeability and proton conductivity.

Mauritz research group studied preparation of Nafion/(organically modified silicate) (ORMOSIL) nanocomposites previously.\(^4,5\) By using other silicate precursors (i.e., diethoxydimethylsilane (DEDMS), phenyltriethoxysilane (PTES)) or mixed precursors than TEOS, the prepared silicate particles would show different morphology and functional groups on particle surface. Therefore, preparation of sSEBS/ORMOSIL nanocomposite membranes could afford broad possibility to optimize properties for polymer electrolyte membranes.

Dynamics of sSEBS/Silicate by BDS

In this research, BDS was proved a powerful tool in study of block copolymer dynamics. It is suggested to study dynamics of sSEBS/silicate composites by BDS in the future. The sSEBS/silicate nanocomposites have more complicated morphology than pure sSEBS. The effect of silicate introduction on dynamics of sSEBS matrix and possible interfacial polarization, arising from interface between polymer phase and silicate particles, would be major concern for this future study.
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