ABSTRACT


Block copolymers (BCs) have remained at the forefront of materials research due to their versatility in applications ranging from hot-melt/pressure-sensitive adhesives and impact modifiers to compatibilizing agents and vibration-dampening/nanotemplating media. Of particular interest are macromolecules composed of two or more chemically dissimilar blocks covalently linked together to form triblock or pentablock copolymers. If the blocks are sufficiently incompatible and the copolymer behaves as a thermoplastic elastomer, the molecules can spontaneously self-assemble to form nanostructured materials that exhibit shape memory due to the formation of a supramolecular network. The BCs of these types are termed as conventional. When BCs contain blocks having ionic moieties such as sulfonic acid groups, they are termed as block ionomers. Designing new systems based on either conventional or ionic BCs, characterizing their structure-property relationships and later using them as electroactive polymers form the essential objectives of this work.

Electroactive polymers (EAPs) exhibit electromechanical actuation when stimulated by an external electric field. In the first part of this work, it is shown that BCs resolve some of the outstanding problems presently encountered in the design of two different classes of EAP actuators: dielectric elastomers (DEs) and ionic polymer metal composites (IPMCs). All-acrylic triblock copolymer gels used as DEs actuate with high efficacy without any requirement of mechanical prestrain and, thus, eliminate the need for bulky and heavy hardware essential with prestrained dielectric actuators, as well as material problems
associated with stress relaxation. The dependence of actuation behavior on gel morphology as evaluated from mechanical and microstructure studies is observed.

In the case of IPMCs, ionic BCs employed in this study greatly facilitate processing compared to other contenders such as Nafion®, which is commonly used in this class of EAPs. The unique copolymer investigated here (i) retains its mechanical integrity when highly solvated by polar solvents, (ii) demonstrates a high degree of actuation when tested in a cantilever configuration, and (iii) avoids the shortcomings of back-relaxation/overshoot within the testing conditions when used in combination with an appropriate solvent.

In the second part of this work, two chemical strategies to design midblock sulfonated block ionomers are explored. In one case, selective sulfonation of the midblocks in triblock copolymers is achieved via a dioxane:sulfur trioxide chemistry, while in the other acetyl sulfate is used for the same purpose. Excellent control on the degree of sulfonation (DOS) is achieved. The block ionomers swell in different solvents while retaining their mechanical integrity. They show disorder-order, order-order, and order-reduced order morphological transitions as DOS varies. These transitions in morphologies are reflected in their thermal behavior as well. The microstructures show periodicity, which is, again, a function of DOS. The transitions are explained in terms of the molar volume expansion and volume densification of the blocks on sulfonation. The ionic levels, morphology and periodicity in microstructure are important for applications such as actuators, sensors and fuel cell membranes. The ability to tune these aspects in the ionomers designed in this work make them potential candidates for these applications.
Chemical Modification and Structure-property Relationships of Acrylic and Ionomorphic Thermoplastic Elastomer Gels

by

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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Chemical Engineering

Raleigh, North Carolina

2011

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_______________________________  ______________________________
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DEDICATION

This work is dedicated to my family for their loving support and inspiration in all my endeavors.
BIOGRAPHY

I was born in Pusad located in the state of Maharashtra, India. I completed my high school education from Phulsing Naik Mahavidyalaya, Pusad in 2000 to join the Bachelor of Technology program in Fiber and Textile Processing in University Institute of Chemical Technology, Mumbai, and graduated in 2004. Subsequently, I joined North Carolina State University in August 2005 and completed a dual M.S. program in Textile Chemistry and Chemical Engineering under the direction of Dr. Brent Smith and Dr. Peter Hauser. The title of my thesis was “Preparation of Ionic Cellulose for Wrinkle Resistant Fabrics”. On completion of my M.S. program, in year 2007 I joined the Polymer Morphology Group in the Department of Chemical and Biomolecular Engineering to pursue my Ph.D under the direction of Drs. Richard J. Spontak and Tushar K Ghosh. Following my Ph. D., I will be joining Eastman Chemical Company, Kingsport, Tennessee as an Advanced Research Scientist.
ACKNOWLEDGMENTS

I would like to take this opportunity to express my deepest gratitude to Drs. Richard Spontak and Tushar Ghosh for being the excellent advisers, who helped me hone my research skills and grow both personally and professionally. They gave me the freedom and encouragement needed to pursue research avenues that interested me. Working with them has been a great learning and an enriching experience. I am also grateful to them for being very supportive and understanding in all phases of my life during my stay at NC State.

I am grateful to Dr. Saad Khan for his help and advice in my research and for serving on my committee. I would like to thank Dr. Michael Dickey for being on my dissertation committee, for sharing his research ideas and including me in the brain-storming sessions with his group members.

My special thanks to Dr. Klaus Tauer, who gave me the opportunity to visit his lab in Germany and taught me the sulfonation chemistry and later helped me in characterization of the ionomers. I would like to express my gratitude to Dr. Steve Smith from P&G for synthesizing block copolymers required for my sulfonation experiments. My thanks to Drs. Robert Weiss and Bruce Novak for their advice and inputs in my ionomer chemistry projects. I would like to express my appreciation to Dr. Christopher Gorman for accommodating me in his lab for all my synthesis experiments. Thanks to Dr. Ewellyn Capanema for providing the access to lyophilizer in her lab for some of my experiments.

I would also like to thank the National Science Foundation and the Department of Chemical and Biomolecular Engineering for funding my research during my program. I have been very fortunate to be a student in this department and, especially, a member of the
Polymer Morphology Group. The group members were always helpful in my experiments and were a great source of new ideas. My sincere gratitude to my group members Arjun, Kristen, Evren, Anand and Xiao Jing, who not only were great colleagues but at times went out of their way to help me in my endeavors. Many thanks also to the members of Dr. Ghosh’s lab—Aylin, Partho, Krishnabala, Saral and Anees and Dr. Khan’s lab—Sara, Alina, Mohammed, Chris and Christina for help with various experiments. I acknowledge members of the Gorman group—Molly, Janelle and Kaitlyn— who helped me in running the chemistry experiments.

My stay at NC State has given me friends who made my stay enjoyable and memorable. I would like to thank my room-mate Jaspreet for being very understanding and supportive during all these years and not to forget, his delicious food. I would like to acknowledge my friends Prashant, Dnyanada, Abhishek, Loganathan, Narendiren, Prasenjeet, Prachi, Khushboo, Priya, Mehmet, Rajendra, Sumit and Nimish for all the good times.

My success and achievements would be incomplete without the support and blessings of my parents and family. My sincerest gratitude to my brother Gitesh, sister Aditee and to my parents, whose love and affection has helped me sail this far. And finally, thanks to Lord Gajanan for his blessings.
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reported for hydrated IPMCs composed of an endblock-sulfonated triblock copolymer (○) at 1 V\textsuperscript{19} and Li-exchanged Nafion\textsuperscript{®} (dashed line) at 1 V and 0.5 Hz\textsuperscript{19} and Na-exchanged Nafion\textsuperscript{®} (△) at 2 V\textsuperscript{30} are included. (d) Bending actuation as a function of time for IPMCs consisting of GLY-solvated PBI (labeled with the cation and applied voltage) and Nafion\textsuperscript{®} (labeled with the cation in parentheses) at 2 V.\textsuperscript{26} (e) Bending actuation as a function of time for IPMCs consisting of EG-solvated PBI (labeled with the cation and applied voltage), as well as Nafion\textsuperscript{®} (△, ◊) and Flemion\textsuperscript{®} (□) (each labeled with the cation and applied voltage in parentheses).\textsuperscript{26} In both (d) and (e), the effect of Pt coating on bending actuation is shown for PBI-based IPMCs (○, labeled with the number of Pt cycles) at 7 and 1 V, respectively. The dashed lines in (d) and (e) serve to connect literature data, whereas the solid lines correspond to regressions of Eq. 1 to data collected here. The bending direction of the IPMC is identified by the background shading: anode (white) or cathode (gray). (f) Values of \( D_m \) extracted from the regression analyses in (d) and (e) and presented as a function of electric potential for PBI-based IPMCs solvated with GLY (circles) and EG (triangles) and subjected to 2 (filled) and 3 (open) Pt deposition cycles. The solid and dashed lines in (f) serve to connect the data......188 Figure 6.4 Maximum bending actuation achieved for IPMCs fabricated from the PBI investigated in this work. Shown here are the IPMCs with GLY (filled symbols) and EG (open symbols), each labeled with the number of Pt deposition cycles. Error bars correspond to the standard error. The cross-hatched region identifies the range of actuation levels achieved for conventional IPMCs under similar test conditions. Background shading is the same as in Fig. 6.3, and the solid lines serve to connect the data. ..............................................190
Figure 7.1 Shown in (a) typical $^1$H NMR spectra of neat SBS denoted as ‘00’ and sulfonated ionomer with highest level of sulfonation indicated as ‘81’. The solvent peaks are labeled. The aromatic band, the aliphatic band due to protons in unsaturated butadiene units and the aliphatic polymer backbone zone are labeled. In (b) expanded spectra between 4.5 and 7.5 ppm. The ionomers are labeled with numbers corresponding to their degree of sulfonation. Neat SBS was tested in THF solution, while the ionomer in solvent mixture of THF and water mixed in 3:1 ratio. The spectra are shifted vertically for convenience.

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Figure 8.6 Expanded spectra between 400 and 1000 cm⁻¹ for the spectra shown in Figure 4. Variation in intensities of the labeled peaks indicated sulfonation levels.

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1 Dissertation Overview

Designing new block copolymer (BC)-based systems, characterizing their structure-property relationships and demonstrating their use as electroactive polymers (EAPS) form the essential objectives of this work. The dissertation is broken into six main chapters that explain these objectives and the obtained outcomes in details.

Chapter 2: This chapter is essentially a review of literature available on the block copolymer systems used as electroactive polymers, specifically, as dielectric elastomers (DEs) and ionic polymer-metal composites (IPMCs) that constitute two different classes of EAPs.

Chapter 3: This chapter discusses the mechanical behavior of ternary blends of styrenic diblock and triblock copolymers with mineral oil and its effects on electroactuation behavior.

Chapter 4: In this chapter all-acrylic triblock copolymer gels are investigated to evaluate their morphological and mechanical properties and electroactuation behavior as DEs. The properties are correlated that explain the trends seen in electroactuation.

Chapter 5: In this chapter, we report on the versatility of the selectively solvated networked BC systems for use as DEs and IPMCs. Different systems comprised of solvated triblock and
pentablock networks are highlighted to emphasize their potential in serving as tunable actuation behavior.

Chapter 6: We present IPMCs discussed in Chapter 5 in great details and demonstrate their facile fabrication, actuation efficacy and tunability in actuation performance by varying parameters such as solvents used and electric potential applied.

Chapter 7: The midblock sulfonated ionomers of poly(styrene-\(b\)-butadiene-\(b\)-styrene) are reported. This chapter covers the synthesis strategy, chemical characterization, thermal and morphological behavior of these ionomers.

Chapter 8: The methodology for selective sulfonation of the styrene block in a poly[(\(p\)-tert-butylstyrene)-\(b\)-styrene-\(b\)-(\(p\)-tert-butylstyrene)] copolymer is described. A detailed discussion on the observed properties and evolution of morphology with sulfonation is provided.

Chapter 9: Conclusions

Chapter 10: Recommendations for future work are made.
2 Block Copolymer-based Systems: An Emerging Materials Platform for Electroactive Polymers

2.1 Introduction

The ensemble of soft polymer-based stimuli-responsive materials (SRMs) providing functionality in response to stimulus such as temperature, pH, radiation, electric potential/field, reagent concentration has enriched in recent years. The functionality could be measured, for example, in terms of changes in various parameters such as shape (deformation), color and flow. When electric potential/field is utilized to achieve deformation and vice-versa in polymers, these SRMs can be termed as electroactive polymers (EAPs). They fall in the broad category of ‘smart materials (SMs)’ that include shape memory alloys (SMAs), magnetostrictive alloys (MAs) and piezoelectric ceramics (PCs). The EAPs offer a set of properties, not seen in any one standalone SM, that are critical when considering their applicability as biological replicas. To enunciate, the EAPs, unlike SMAs that take long actuation time per cycle due to heating and cooling processes involved, can be operated at higher actuation frequencies, and dissimilar to MAs and PCs are distinctly soft and produce high actuation strains. The focus of recent research endeavors has been on using EAPs as artificial muscles.

The EAPs outperform conventional actuators comprising of combustion engines and electric motors in designing an artificial muscle in that they do not require complex transmission systems to operate, are energy efficient, lightweight, cost effective and are easy
to manufacture. They are less noisy, generate less heat and are compliant thus providing the “give” seen in natural muscle. The EAPs also compare well in terms of actuation strain and energy densities. The need for natural muscle-like materials is realized more than ever in the absence of actuators that can replace failed or weakened muscles. Muscle-like technology would be beneficial in medical implants and human-assist devices and could prove imperative in simplifying surgical procedures and diagnostic tools. Apart from biomimetics, EAPs can be further used as loudspeakers, transmission gratings, diffraction gratings and optical zoom lenses that can be integrated into current day robotics technology for designing humanoids possessing speech and vision capabilities. Additionally, these materials can be used in prosthetics, haptic devices such as refreshable Braille touch-screens, devices such as wipers and grippers to perform mechanical work, microfluidic devices such as micropumps and wearable tactile interfaces and micro vehicles for monitoring and surveillance.

The EAPs are broadly classified into two classes based on their mechanism of deformation: electronic and ionic. Electronic EAPs include dielectric elastomers (DEs), ferroelectrics and liquid crystal elastomers, whereas ionic EAPs include ionic polymer-metal composites (IPMCs), carbon nanotubes and conducting polymers. Relative merits and challenges associated with these EAPs for their use as artificial muscles and other applications are published in several elaborate reviews. While the readers are requested to refer to these articles for more details on contemporary materials used for each of these EAPs and their properties, we would like to henceforth focus on DEs and IPMCs with emphasis on block copolymer-based material systems that have recently been introduced and show tremendous potential as EAPs for several applications in near future.
Block copolymers (BCs) consist of two, three or multiple homopolymeric blocks linked to each other by covalent bonds. They are capable of self-organizing into a variety of morphologies based on the architecture, composition and molecular weights. For example, diblock and triblock copolymers of ABA architecture can microphase separate into classical morphologies such as lamellae, cylinders on a hexagonal lattice, spheres on a body-centered-cubic lattice or discontinuous morphology such as gyroid (Figure 2.1).4 Multi-block copolymers of ABC and ABCBA can have more complex morphologies in addition to the ones mentioned above (Figure 2.2).5,6 When the block size is > 2 and at least two of the blocks are glassy at room temperature and contain a rubbery midblock between them, the copolymers can form networked structures that have shape memory attributes. The properties and morphologies of these BCs are widely tunable with the addition of solvents and/or homopolymers. The physically cross-linked networks of the similar type are used as EAPs and form the focus of this paper.

2.2 Dielectric Elastomers (DEs)

Dielectric elastomers are insulator materials that use high electric fields to actuate (deform) with near-zero current requirements, are fast operating and produce large strains (> 100%). Typically, a DE consists of an insulator elastomeric film sandwiched between two compliant electrodes forming a capacitor arrangement. When an electric field is applied, the oppositely charged electrodes attract each other compressing the essentially incompressible elastomer in thickness direction at the active area (area with electrodes), due to compressive
Maxwell stress, which then increases in planar area. Voltage requirements are as high as 500 V to 10 kV for an elastomer of about 10 to 100 μm thickness. The change in active area is measured in terms of strain and termed as DE actuation. The strain also generates an output force which is another metric to measure actuator performance. The force is the maximum when actuation strain is zero and decreases as the strain increases. It is this deformation and force (stress) that can be used to perform mechanical work when DEs are used in the form of artificial muscles and/or prosthetics in biomimetic systems, for lens and mirror adjustments in space applications, as Braille devices for generating refreshable characters, microfluidic devices, diaphragms and pumps, tunable diffraction gratings etc.

A variety of materials that includes mainly silicones, acrylics and polyurethanes (PUs) have been used as dielectric elastomers. A comprehensive list of the different materials used as DEs is provided by Brochu and Pei.\textsuperscript{1} Pelrine et al.\textsuperscript{7} reported that with the application of biaxial prestrain the acrylic and silicone can actuate to trigger strains greater than 100%. Though the mechanism of this improvement remains uncertain, it has led to keen interest in these materials in the scientific community. Prestrain increases the breakdown electric field (the electric field at which the material no longer remains an insulator and starts conducting) and reduce viscoelastic effects, more in silicones in the latter case. Acrylic elastomer VHB films from 3M have been most widely used as DEs for research and applications. They produce strains of 380% and above and impressive energy density of 3.4MJ.m\textsuperscript{-3}. Polyurethanes produce large forces, but limited actuation strains, at low electric fields due to their high dielectric constant. Silicones being less viscoelastic in nature can be used at high frequencies producing low viscous losses. However, they produce strains lower than acrylics
and need high electric fields due to their low dielectric constants. These materials, being derived from physically crosslinked homopolymers, present difficulties with regards to size/shape customization, reusability and property tunability, both, mechanical and electromechanical.

As alluded to above, a mechanical prestrain can improve the actuation performance. Not only this, it also improves the mechanical efficiency and response speeds of DEs. DEs actuate and finally fail at an electric field called breakdown field in defective areas in the elastomer. These defects could be from steps involved in manufacturing, processing and/or sample preparation for actuation. Prestrain is believed to reduce the pull-in effects, one effect due to which DEs fail, and hence improves the breakdown electric fields. It also improves the frequency response by reducing viscoelastic effects, noticeably in acrylics. Prestrain can also be used to introduce selective anisotropy in actuation by prestraining in one direction more than the other. However, prestrain has certain disadvantages. First, it reduces dielectric constants necessitating the need for high electric fields for actuation. Second, to hold prestrain in place, rigid frame structures are required that adds to the weight of the device reducing its work density and power/mass ratio. Also, with time the prestrained films can undergo stress relaxation or get fatigued causing the device failure.

To reiterate, the conventional DEs derive from chemically crosslinked homopolymers that offer little versatility in terms of property tenability, shape/size customization, material stability and reusability. They suffer from issues of high electric field requirements that demand employing heavy power supplies in a device and consequently make prestraining of the elastomer unavoidable to keep the field for actuation low. Prestrain leads to several
problems listed above. There is an impinging need for new materials that help resolve these issues with DEs. Block copolymer-based materials come forth as a new class of materials as a step in this direction. These materials are have physical crosslinks forming three-dimensional networks and have illustrates a strong candidacy as DEs. In this review, we highlight key developments in the use of these materials as DEs.

2.2.1 Block copolymer-based DEs (BCDEs)

Thermoplastic organogels comprising of an ABA type elastomeric triblock copolymers and a B- block selective solvent have found wide applications that range from consumer and personal care products to adhesives and shock-absorbent media in sports goods. The elastomer is different from homopolymeric elastomers in that, unlike the latter, they are physically, not chemically, crosslinked due to glassy A micelles that are connected via rubbery B blocks. An interesting application of these materials, reported in the last few years, is as electroactive polymers, more specifically as dielectric elastomers. To distinguish them from homopolymers they were termed as electroactive nanostructured polymers (ENPs) due to their microphase separated morphologies with nanosized block domains. As a first system a non-polar macromolecule of poly[styrene-\(b\)-(ethylene-\(co\)-butylene)-\(b\)-styrene)] (SEBS) swollen with a midblock (EB) block selective aliphatic mineral oil (MO) was used, where the block copolymer molecular weight and concentration was varied to investigate the tunability in electromechanical properties. Three different molecular weights of BCs, 75, 161 and 217 kDa, abbreviated as ENP75, ENP161 and ENP217, with about 30-33% S content were used.
Readers are directed to read ref 8… for sample preparation methodology. The different compositions made with MO of the copolymers were tested for mechanical and electromechanical properties.

As mentioned earlier, actuation of DE occurs due to the generation of Maxwell stress between the electrodes that form a capacitor arrangement. Maxwell stress given by

\[ \sigma_m = \varepsilon_0 \varepsilon E^2 \]

Equation (1)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the material dielectric constant and \( E \) is the applied electric field, emphasizes that the electric-field-induced actuation depends on dielectric constant (\( \varepsilon \)) of the DE. The value of \( \varepsilon \) decreases for silicones and acrylics with frequency which could be a disadvantage for applications where high frequencies are required during actuations. In the case of SEBS system, \( \varepsilon \) remains independent of frequency and is lower in magnitude than either silicones or acrylics (\( \varepsilon = 2-4 \) and 4-5 respectively).

Figure 2.3 shows the dielectric constants for different compositions for ENP161 and 217 series and compares those values for silicones and acrylics. Based on equation (1), it is anticipated that the actuation for these materials would be lower than the conventional materials at a given electric field (below the breakdown field). However, it should be noted that actuation is sensitive to the mechanical properties of the materials along with \( \varepsilon \). By varying the amount of oil in the composition the properties such tensile moduli can be tuned. Figure 2.4 obtained from measuring moduli from uniaxial tensile testing indicates this effect for all the molecular weights. The compositions with low moduli are less stiff and actuate
more at a given electric field. The molecular weight decided the lowest concentration of copolymer that can impart mechanical stability to the composition in the form of a film. For example, in the case of ENP75, this concentration was ~20 wt %, whereas for the other two BCs it was ~5 wt %. The moduli values were seen to be consistently lower than the crosslinked homopolymers. Another aspect, critical to DE performance, is hysteresis from repetitive cycling in application. This can be deduced, again, from tensile testing. When cycled at 400% strain for 100 cycles, the hysteresis for this networked materials, depending on compositions, were observed to be less than 18 %, which for acrylic elastomer under similar conditions was 38%.

Because of the lower rigidity of compositions with ENP161 and ENP217, only they were tested for actuation and actuation strain, denoted by $S_{act}$, were reported (cf. Figure 2.5). The actuation strain ($S_{act}$) was calculated by measuring the change in active electrode area laterally under electric field and normalizing it with the initial area before actuation. Figure 2.5 shows that copolymer concentration and molecular weight have systematic effect on electromechanical response of the ENP networks. For both molecular weights, at low copolymer concentrations (and hence at low corresponding moduli), $w_{BC}$, actuation was ultrahigh (> 200%, maximum of ~ 250%) and was achieved at electric fields as low as 20 kV/mm. As $w_{BC}$ increased, $S_{act}$ decreased with a corresponding increase in dielectric breakdown field (Figure 2.6). At low $w_{BC}$, there are fewer copolymer chains available for network formation and the matrix mainly comprises of the selective solvent, oil, which was suspected to dominate the dielectric breakdown. At the lowest $w_{BC}$ examined, the actuation performance is superior compared to acrylics and silicones. The ultrahigh actuation has been
ascribed to the inherent polarizability of styrene rings under the electric field, though conclusive investigation is still pending.\(^9\) Also, the possibility of micelle deformation due to prestraining, done before actuation was also suspected to be an important consideration in these materials and has been recently evaluated by Krishnan et al\(^{10}\) by small angle X-ray scattering (SAXS). The authors reported that spherical micelles deform into ellipsoidal shapes with eccentricities of about 0.42 under prestrain and further provided a molecular level understanding of the micellar coronal interactions in SEBS gels when biaxially stretched. Kim and coworkers, while studying SEBS (Kraton G1650)/MO gels having 70 wt\% MO with, recently reported that under the electric field the \(d\)-spacing between the micelles decreases in conjunction with the deformation in DE thickness direction thus confirming that these materials are vastly incompressible and undergo affine deformation.\(^{11}\) The high molecular weight ENP217 series consistently attained greater strains exhibiting larger electromechanical response than ENP161 blends due to its lower moduli. Conversely, the ENP217 series displays lower breakdown fields (\textit{cf.} Figure 2.6) likely from the mechanical breakdown of the elastomer due to thinning in thickness during actuation.

Other metrics that measure the DE performance are electromechanical coupling efficiency \((K^2)\) and energy density \((F)\). The \(K^2\) is defined as the ratio of mechanical energy stored to the electrical energy supplied, whereas \(F\) measures the work generated per actuation cycle per unit actuator volume. For high actuation strains \(K^2\) is given by 
\[-2s_z - s_z^2\] and \(F\) by 
\[-\sigma_m \ln(1 + s_z)\], where \(s_z\) is the transverse strain calculated from the initial film thickness and empirically measured actuation strains. The highest \(K^2\) of 92 \% was shown by ENP217 system containing 5 wt\% copolymer. The efficiencies decreased with the
copolymer molecular weight and increasing polymer concentrations (in the examined range). The $F$ values vary inversely with $S_{\text{act}}$ and $K^2$. They compare well with those determined for silicone elastomers, however, are lower than acrylic elastomer. The ENP75 series, due to its intrinsic rigidity was actuated without any prestrain and was seen to outperform acrylics, tested under similar conditions, in terms of actuation strain and energy density (Figure 2.7). The strains achieved were about 2.5 times and $F$ values were about 5 times compared to acrylics. Two more block copolymer-based systems comprising of triblock copolymers—poly[styrene-\(b\)-(ethylene-\(co\)-propylene)-\(b\)-styrene)] (SEPS) and poly[styrene-\(b\)-(ethylene-\(co\)-[ethylene-\(alt\)-butylenes])-\(b\)-styrene)] (SEEPS)—solvated by MO have also been reported, in which case SEPS/MO series showed strains of up to 300%. The $F$ values were at 1.5 MJ m\(^{-3}\) that were higher than those ascertained for SEBS/MO compositions. The increase was most likely due to changes in chemistry and associated physical attributes. A much broader property change and tenability was reported when different midblock selective solvents were used.

Using different midblock selective solvents not only help in tuning actuation strain alone, but also properties such as $F$ and blocking stress. The blocking stress is defined as the force required for bringing a fully actuated DE to zero displacement and hence provides a measure of how much of force it can exert to move an object. A hydrocarbon tackifying resin was used as a selective solvent for a SEBS copolymer (265 kDa, 33 wt% S). The $F$ value was 8MJ m\(^{-3}\) and blocking stress of 700 kPa was realized. This blocking stress exceeded the values that a mammalian muscle can generate (~ 550 kPa). However, with resin as a solvent, the response to the electric field is slow and recovery as well is sluggish. Mixing MO with
resin as a selective solvent, the material demonstrated the potential for tunability of time scales required for actuation response (Figure 2.8). For example, two extreme responses were seen when alone MO or resin was used as a solvent and tested for actuation at two fixed (low and high) electric fields. With MO as a solvent (70 wt%), at both electric fields the actuation initially occurred rapidly in ~1 S followed by a slow response later until, in most cases, the material failed due to thinning. For the case of resin actuation started slowly and increased thereafter to field-dependent values. When MO and resin was mixed in different ratios, intermediate responses were observed. The ability to tune the actuation response over a period of time in a controlled manner opens several avenues of applicability for these materials, for instance, in time switches.

The electric field reported in most of the literature for DE actuation use nominal electric field that is obtained by dividing the applied potential with the thickness of the prestrained film to be actuated. For comparative purposes and reproducibility, this is considered sufficient. Recent findings by Krishnan et al. indicate otherwise. The authors suggest that it is critical to independently consider the film thickness before and after the prestrain. In their studies, different composition of SEBS/MO were made into films of different thicknesses and tested with different prestrains. At a constant prestrain, the trends in actuation across different compositions compared differently when film thicknesses were different. For example, in Figures 2.9a and 2.9b film thicknesses of 1.8 mm and 3mm (before prestrain) were respectively tested for actuation at a prestrain of 300%. In Figure 2.9a as the copolymer content increased (and hence the modulus), maximum actuation increased, whereas the opposite trend was seen in Figure 2.9b Thus, actuation was suggested to depend
on the material (SEBS/MO) composition and process parameter, thickness, in this case. To
determine the extent and cause of this coupled dependence, the authors first reanalyzed the
actuation data by defining a new characterization parameter termed as electromechanical
modulus. This parameter eliminated the inconsistencies arising from comparing different
systems based on their ultimate properties as well as the ones resulting from minor variations
(such as initial film thicknesses) in specimens within a system resulting from processing.
Maxwell stress developed during actuation was calculated by using the instantaneous true
thickness of the films as actuation proceeded, which was then plotted against the transverse
strain. Figures 2.10a-c depict the responses for films of 1.8mm thickness and varying
prestrains (in %) of 100, 200 and 300. The electromechanical curves mimic the stress- strain
responses obtained from the purely mechanical compression tests. At low strains, the
responses were linear, the slopes of which provided the electromechanical moduli. When the
curves in Figures 2.10a-c were normalized by the corresponding electromechanical moduli
(Figure 2.11), all the curves fall on a master curve indicating that the undermining actuation
mechanism is more or less independent copolymer concentration in the concentration range
explored.

In order to determine the effect of film thickness before prestrain on actuation, a fixed
composition (of 25 wt % SEBS) was used to prepare films of different thicknesses and then
tested with prestrains of 100, 200 and 300 (%) (cf. Figure 2.12). It was concluded that the
initial film thickness does not influence the shape or nature of electromechanical response.
However, when deformations were compared at different prestrains (Figure 2.12a-c), a clear
effect of prestrain on actuation response was seen. Actuation response expressed in terms of
dielectric breakdown and ultimate actuation strain showed evidence of influence of film thickness on actuation. Above a film thickness of 0.5 mm, dielectric strengths increased with prestrain and copolymer concentration in line with the combined effect of increasing rigidity of these copolymer-based DEs with increasing prestrain that delay the pull-in failure, if they exist, and likely dominance of breakdown strength by the increasing copolymer (as contribution from MO decreased) fraction in the composition (Figure 2.13), in line with the previous observation. At 0.5 mm film thickness, this trend was not evident likely due to film defects, the effect of which cannot be neglected in thin films as it can aid in catastrophic failure in transverse direction. This effect gets further magnified as prestrain is applied. In the case of thicker films, the defects need to be aligned in order to suffer such a catastrophic failure.

When variation in actuation strain is considered (Figure 2.14) as the prestrain is kept constant and copolymer concentration and film thickness is systematically varied, two regimes were observed. In the first regime, as the thickness increased, almost independently of copolymer composition, the actuation strength increased. Again, this was attributed to the reduced influence of defects in thicker films that resulted into higher electric fields and hence higher actuations. In the second regime, the actuation strain broadly decreased as films became increasing stiffer as copolymer concentration increase. Even when thicker films, about 3 mm thick, were prestrained to 300%, the required electric fields for the stiffer films to obtain actuation were extremely high that lead to surface charging and sample heating causing premature failure. In the final set of their experiments, Krishnan et al. tried to decouple the effect of thickness and prestrain on actuation. For varying copolymer
concentrations, thicknesses and prestrains were chosen such that the final thickness, which is the same as used to calculate the electric field during actuation, after prestrain remains constant. Unlike the expectations, for a given copolymer composition, maximum actuation strain achieved was found to depend on prestrain indicating that the system behavior is much more complex to evaluate even when the film thickness is kept constant. The actuation tests were further performed at a fixed electric field. The achieved actuation, contrary to expectations, demonstrated nearly linear variation, that is, with increasing prestrain the actuation decreased for any copolymer concentration. This indicated that increased polymer stiffness resulting from applied prestrain could be playing a critical role in determining the actuation and emphasized that electric fields expressed in terms of initial thickness (after making adjustments for prestrain) is not sufficient for comparing across systems.

A concern with DEs, in general, is the need for noticeably high electric fields for actuation. One route to overcome this problem— that has been widely explored in conventional DEs— is to increase the permittivity or dielectric constants of the elastomers. Kofod et al.\textsuperscript{15, 16} investigated SEBS (without any MO) and reinforced it with a variety of fillers. The first set of fillers included incorporation of coated/non-coated TiO\textsubscript{2} nano particles. The composites with non-coated TiO\textsubscript{2} particles showed improved permittivity at the cost of poor mechanical properties. When coated TiO\textsubscript{2} particles were used and loaded 30 vol % \( \varepsilon \) increased by 3.5 times. Actuation strain remained constant at 15 vol% loading though the required electric field reduced by about 27% (Figure 2.15).\textsuperscript{15, 17} At higher loading, the breakdown strengths decreased primarily assigned to defects in the composite due to improper mixing at high TiO\textsubscript{2} concentrations. Carbon black was the second type of
reinforcement that was incorporated into the SEBS matrix. Initially, as the amount of the filler increased up to 4 vol%, the permittivity as a function of frequency, which for neat SEBS was independent, increased by about an order of magnitude and then showed frequency dependence at higher loadings. At higher loadings, huge dielectric losses were seen indicating that the composite is near percolation threshold at 4 vol%. As the permittivity increased the breakdown field decreased due to increased defects in the composite arising from TiO₂ inclusion. Figure 2.16 weighs the observed increases in permittivity values against the reductions in breakdown fields. In the third case, a special SEBS with maleic anhydride (MA) functionality was used to graft a conducting polyaniline (PANI) up to 2.3 vol%. Similar to the case of carbon black composites, two regions were seen for permittivity. In the first region, the real component remained independent of frequency, while in the second region it increased with grafting and strongly depended on frequency (Figure 2.17). The breakdown field in region 1 remained constant, same as for neat SEBS, and then dropped in region 2. The steady breakdown electric fields translated into high energy densities (Figure 2.18). The reduction in breakdown field in region 2 was compensated by increase in permittivities to yield high energy densities. At very high grafting densities (2.8 vol%), the actuation strains were low.

The concept of using a triblock copolymer elastomer system as DEs is not limited to styrene- diene type of elastomers and can be extended to other block copolymer chemistries that have shape memory attributes and can be strained to a few hundred percents to recover completely when the stress is removed. A triblock copolymer of poly[methyl methacrylate-b-n-butyl acrylate-b-methyl methacrylate] (MBM) solvated by a midblock selective
solvent- dioctyl phthalate (DOP)- showed remarkable actuation strains of nearly 110% (Figure 2.19a), and that too with no requirement of prestrain. These values are about 5 times higher than those seen for SEBS ENP75/MO compositions tested under no prestrain conditions.\textsuperscript{12} No fillers were required, as in the case of Kofod \textit{et al.}\textsuperscript{16} due to inherent high dielectric constants (of up to 4.2) of the blends. Absence of fillers bars any compromises in reduction of breakdown electric fields due to defects arising from mixing and filler- matrix interface interaction. Actuation without prestrain eliminates all the disadvantages, of bulky framework required to hold the prestrain in place and stress relaxation of the DE with time, that were described previously. The actuation response for these materials were broadly tunable as in the case of styrenic block copolymers and were well described by recent models as described by Zhao and Suo\textsuperscript{18} (\textit{cf.} Figure 2.19b). These DEs yielded electromechanical $k^2$ values of up to 80% and $F$ values of $\sim$ 50 KJ m$^{-3}$. The ascertained values of actuation strain, $k^2$ and $F$ are higher than that (40%, 40% and 8 KJ m$^{-3}$ respectively) demonstrated by a mammalian muscle. The $F$ values were about twice of SEBS ENP75/MO series.

2.3 Ionic Polymer Metal Composites (IPMCs)

Ionic polymer metal composites are low voltage, slow operating, low-power devices that actuate to produce smaller strains ($<10\%$) and can be used in applications where large forces or high operational frequencies are not required. IPMCs typically consist of an ion containing membrane film that is coated with metal electrodes on two surfaces that when subjected to electric potential in cantilever configuration lead to bending deflections. This is
termed as IPMC actuation (Figure 2.20). Conversely, bending IPMC can induce current flow, which can be used for sensing motion and energy harvesting. Constant voltage or current conditions can be used to precisely position the bending deflection without the need of bulky machinery required in electric motors. The device can function as a motion-control device and as well, as a sensor. Some other interesting applications of IPMCs include gates in microfluidics, prosthetic grippers in robots, wipers for space rovers, camera apertures, vibration sensing devices and artificial muscles.

The IPMCs show a bending actuation that is induced by a capacitive flow of ions and solvent under the influence of applied electric potential. The ions could be mobile cations/anions in the membrane. The mobile charges are balanced by a fixed number of counterions that are covalently bound to non-polar polymer backbone. The hydrophilic ionic sites microphase separate from the hydrophobic backbone forming ionic domains that are suspected to be connected via nanosized ionic channels forming what is called as a cluster network. This network is capable of ion transport in the presence of a solvent. The anionic membrane film with electrodes when subjected to electric potential (of < 10V depending on solvent), solvated cations move towards cathode entering clusters in that region and swelling it, thereby generating electro-osmotic pressure. The anode region being depleted of solvent de-swells. In cantilever configuration the IPMC bends towards anode. This actuation mechanism is the most widely accepted mechanism amongst the several that are proposed. Recently, Park et al. have provided a direct experimental evidence of this mechanism in Nafion®-based IPMCs by the neutron imaging technique.19 The performance of IPMCs can be quantified under zero displacement or zero load conditions. Under the first state the
blocking force generated is measured, whereas in the second tip deflection is noted. Often, IPMCs show back relaxation, that is, it deflects backwards towards its original start position after reaching a maximum deflection while still being subjected to electric potential. The reason for this phenomenon is not clear so far and several theories are proposed to explain this behavior.²⁰, ²¹

IPMCs have three main components: the ion-containing ionomer membrane, high surface area electrodes of high electrical conductivity on surface and a polar solvent to conduct ions. The combination of three components decides the performance of IPMCs, and their specific applications.²² The ionomer needs to have a certain elastic modulus (~50 MPa, based on Nafion® membrane²³, ²⁴ and sufficient ionic conductivity in order to achieve electromechanical coupling. These properties are critical as they respectively are responsible for providing structure to the membrane and causing ion transport under applied electric field. A choice of values for these properties decides the bending displacement of the actuator and the force it can generate that in turn decides the application. The device once fabricated is intended to be used for millions of cycles of actuation during which the ionomer film needs to be stable under operating conditions when it is in contact with electrodes and solvent²⁵ and subjected to electric field. The current operating surroundings include open air, submerged state in various liquids, varied humidity, temperature and applied potential conditions. The ionomer must also be capable of containing a solvent and must demonstrate chemical stability during electrode fabrication by chemical methods. The morphology and the mechanical properties of the ionomer such as Nafion® by Dupont have been found to match several of these required properties and hence it serves as a benchmark material for
IPMCs. Nafion® is hypothesized to consist of microphase separated morphology of hydrophobic semi-crystalline domains of polytetrafluoroethylene backbone (PTFE) and hydrophilic clusters/multiplets of sulfonate functionalities on perfluoroether branches. The semi-crystalline domains provide a modulus of about 100MPa in dry state to the ionomer and about a half in wet state. The tensile modulus scales inversely to the solvent uptake, whereas ionic conductivity is directly related to swelling by solvent and increases as proportion of solvent increases. The clusters are believed to be forming interconnecting channels, as described earlier that facilitate ion transport in presence of solvent demonstrating conductivities of the order of 100mS/cm. As conductivity increases, bending actuation and blocking force also increase. The ionomer needs to be easily processable in melt or in solution to produce dimensionally customized IPMCs and to facilitate device fabrication by a sequence of physical/chemical methods. In all, the ionomer needs to be stable thermally, morphologically, electrically, chemically and mechanically to be apt for use as IPMCs capable of demonstrating high actuations and high blocking forces. Other than Nafion®, fluorinated ionomers such as Neosepta® by Tokuyama25, Aciplex® by Asahi Chemical, and Flemion®23 and Selemion®27 by Asahi Glass and XUS by Dow Chemical Company28 have also been used for IPMCs.

Apart from the microstructure, morphology29 and composition of the ionomer23, 29-33, the actuation behavior of IPMCs widely depend on several factors that include electrode morphology34, solvent type and hydration degree35, 36, nature of neutralizing cations23, 32, 37 and applied electric field38. The most widely studied ionomer, Nafion®, remains difficult to reprocess using conventional techniques of solvent casting or melt processing and shows loss
of useful membrane properties when subjected to such treatments. The morphology of Nafion® is still unclear after years of research that offers a challenge in tuning it if it not known to begin with. This tunability can possibly improve ion transport and hence the actuation. The water uptake of Nafion® is about 30wt%, offering a limitation in performance as IPMCs, where the high solvent uptake and later its transport during actuation remain to be key requirements. Also, IPMCs made from this material suffer from the problem of back-relaxation that mars their potential as artificial muscles. To overcome these problems several material designs have been tried one of which has been the use of block copolymers. It is these block copolymers that we will carefully examine in the next section in context to their performance and applicability as IPMCs.

2.3.1 Block copolymer-based IPMCs (BCIPMCs)

Block copolymers as IPMCs remain to be a relatively new set of materials. Wang et al. were the first to use a sulfonated block copolymer of poly[styrene-\(b\)-(ethylene-\(co\)-butylene)-\(b\)-styrene] for IPMCs. The block copolymer (abbreviated as SSEBS) had sulfonated endblocks of poly(styrene). The chemical structure is shown in Figure 2.21. The authors mentioned that block copolymers are attractive for this application as they are inexpensive compared to Nafion® ionomer and their mechanical and physical properties can be regulated by tuning the lengths of blocks.

In their work, Wang et al. obtained a solution cast film of SSEBS and an IPMC was fabricated by forming Pt electrodes on both surfaces by electroless plating procedure. Figure
2.22 a. shows the mud-cracked texture of Pt electrode obtained from the drying process, whereas b. shows the cross-sectional image of the IPMC. In b. Pt particles about 50 nm in diameter were seen to penetrate about 10 μm deep into the film near both the surfaces. The electrode morphology matched very well with that seen generally in Nafion®-based IPMCs.

The actuation measurements were done, both, under DC and AC voltages. Figure 2.23 shows the actuation behavior at different DC voltages. The maximum deflection increased as the applied potential increased. The behavior is consistent with the general characteristics of IPMCs. The deflection was rapid and maximum displacement was about 1.0 mm at 2.0V.

The IPMCs showed back-relaxation which was assigned to the diffusion of water back towards anode, thus assigning the mechanism of actuation to be solvent and ion transport. When the IPMC was subjected to a sinusoidal AC signal of amplitude 1.5V, the current was observed to be synchronous with the applied signal with a maximum value of about 400mA. However, the tip displacement showed a lag indicating (Figure 2.24) that there is some response time due to the capacitive characteristic of the IPMC. The maximum deflection obtained was about 0.2 mm, which was much lower than 0.5 mm seen for Nafion®-based IPMC at 1.0V AC voltage of frequency 0.5 Hz. As the cation type remains unknown in the case of SSEBS, this comparison should however be only considered qualitatively.

To improve the performance of SSEBS as IPMC materials, Wang et al. further modified the ionomer by incorporating carbon nanofibers (CNFs). About 2.5 wt% loading of CNF was achieved into the ionomer by ultrasonication and eventually evaporating a solvent to obtain nano-composite samples. These CNF-SSEBS films were then fabricated into IPMCs similarly as in the case of SSEBS. The electrodes showed cracks (Figure 2.25)
and were about 10 μm deep on both surfaces as confirmed from cross-sectional SEM. The authors claimed that the distribution of CNF was homogeneous in the SSEBS matrix (Figure 2.26) and images a single nanofiber that appeared like a bamboo structure (Figure 2.27). Compared to SSEBS system alone (Figure 2.28), IPMCs made from CNF-SSEBS composites showed almost two times higher displacement at 2.0 V, faster response and no back-relaxation. The maximum deflection of about 2.8mm was obtained. When sinusoidal voltage input was applied, the tip deflection increases with applied voltage and it decreased linearly with increasing frequency (Figure 2.29). For the sinusoidal wave input, a simple harmonic response was obtained. The mean deflections obtained at different voltages and frequencies were greater in case of the composites than the neat SSEBS. The effect of CNF addition was not only seen in improving the deformation, but also in increased material stiffness and through-thickness conductivity- the properties that subsequently decide the blocking force and deflections.

Wang’s approach of using sulfonated block copolymers showed that these materials show potential as smart materials in the form of IPMCs. There are a few issues that need to be emphasized to fully enumerate the potential of block copolymers such as SSEBS for IPMCs:

1. In the block ionomer such as SSEBS, if the block composition is appropriate, domains of glassy sulfonated polystyrene endblocks into the surrounding matrix of EB block would result from microphase separation of blocks. These domains essentially provide mechanical integrity to the ionomer in the neat form. On introducing a polar solvent such as water these domains get plasticized as the ionic groups get hydrated. Consequently, the material reduces in mechanical strength. If the
ionic content of the polystyrene block is increased, more would be the solvent uptake and more would be plasticization of the glassy domains. High solvent uptake could aid ionic conductivity improving IPMC performance. However, the increased plasticization eventually could lead to mechanically unstable material that is difficult to handle. This makes it necessary that the ionic content is limited to control the solvent uptake.

2. The phenomenon studied by Wang possibly could have been studied by using a sulfonated diblock copolymer of SSEB instead of using expensive triblock ionomers. The triblock ionomers, if needed, could be used for one unique feature that that the diblock ionomers do not offer. Triblocks on microphase separation can form a three-dimensional network-like structure by formation of bridges and loops\textsuperscript{43} that provides improved mechanical properties and shape memory to the materials.

3. As alluded to earlier, block copolymers and ionomers\textsuperscript{44} microphase separate into a variety of morphologies depending on their molecular weights, chemistries and block compositions. The morphology of the microphase separated system has been shown to be to alter the ion transport properties of these materials. By using block copolymers, hence, one can judiciously tune the morphology, thus improving the transport properties and hence the actuation.

Recently, we used a newly introduced block ionomer as a potential candidate for IPMCs. The ionomer had five blocks with the central block— unlike as in the case if SSEBS where the endblocks were sulfonated. The poly\text{[\text{t-butyl styrene-b-(ethylene-alt-propylene)-b-}}
\text{（styrene-co-styrenesulfonate)-b-(ethylene-alt-propylene)-b-t-butylstyrene]} \quad (\text{tbSEPsSEPtbS})
ionomer (from Kraton polymers, Houston, TX) had a molecular weight of 78 kDa (38 wt% tbS, 26 wt% EP (before sulfonation) with 57 mol% midblock sulfonation. Based on the present materials design, we expect that the endblock form glassy micellar cores (cf. Figure 2.30) (depicted as spherical for simplicity), are surrounded by a rubbery shell and reside in a matrix composed of styrenesulfonic acid chains (red dots denote immobilized anions). The micelles are connected by the midblock of EP and sulfonated styrene, thereby forming a mechanically stable network. It is important to note that this ionomer has ionic groups that are present on the central block and any polar solvent introduced will reside in the matrix and will not plasticize the micelles. Depending on solvent, uptakes could be as high as 500% without losing the mechanical integrity of the material. Though we have not varied the ionic content of the ionomer so far, it is possible to do so in order to tune the solvent uptake. Unlike SSEBS, there are no restrictions on ion content of the ionomer and hence the solvent uptake. However, while varying the ionic content precaution must be taken to carefully evaluate the extent of microphase separation and resultant morphology. A film of this ionomer was formed by solution casting from THF and further annealing it under vacuum at 60°C for 24 h to remove any residual solvent. The film was treated to deposit Pt on both surfaces by electroless plating by multiple deposition cycles. To reduce the surface resistance (< 2Ω), silver was deposited on the Pt plated surfaces. The protons were exchanged by Li⁺ ions. When these IPMCs were tested with DC voltage in cantilever form, extensive bending actuations were obtained. Actuation obtained at 1V with water as a solvent was significantly higher compared to the Nafion® and CNF-SSEBS based IPMCs under similar conditions. Tip deflections as high as 3.5 mm were obtained (Figure 2.31). When glycerol was used as a
solvent, actuations were comparable to glycerol solvated Nafion® IPMCs at 2 V. Above 2 V, the actuation was superior (Figure 2.32). The deflection was characterized in terms of L/R or κL, where κ= 1/R, L is the active length of the actuator and R is the radius of curvature of the bent IPMC. The actuation achieved at 7V with glycerol as a solvent is also shown as superimposed snapshots in Figure 2.32. Back relaxation was not observed when glycerol was the solvent. This was assigned to the high viscosity of glycerol resulting into its reduced diffusion towards anode that is supposedly responsible for the backward deflection.

2.4 Broader outlook

The addition of block copolymer-based elastomeric systems to the list of chemically crosslinked elastomers has broadened the matrix of polymeric materials that find utility as EAPs specifically as DEs and IPMCs. The DEs and IPMCs find a variety of applications that each requires a unique set of material characteristics. With the availability of these new materials, it is uniquely possible to tune these EAPs for their mechanical, physical and electromechanical behavior to suit any given application. A glimpse of this possibility in terms of applicability of these materials for some of the applications is provided in this section.

When DEs are to be used for any application, the actuator configuration, along with the inherent actuator performance metrics dictated by the material, becomes an important criterion. The chosen configuration can augment the actuator performance. These configurations include unimorphs, bimorphs, rolls, tubes, spider, bowtie, diaphragms,
stretched frames and extender. A comprehensive account that covers these designs in details and their respective applications is given by Carpi et al.\textsuperscript{45} A number of other configurations have also been reported that includes the one by Kofod et al.\textsuperscript{46, 47}, which is a minimum energy structure having a bendable frame holding the DE that deforms as the elastomer is actuated and then relaxed. Important designs from the perspective of applicability of DEs as artificial muscles are: 1) spring roll and 2) stacked actuators. Both the designs have capability to transform the applied electrical energy into linear actuation. The actuations strains and output forces achieved could be 30\% and 21 N respectively. In spring roll actuators (Figure 2.33), DE is wrapped around the spring, which holds the prestrain in place.\textsuperscript{48} Their main drawback is their premature failure from localized stress concentration in the DE film around the spring and its components. By patterning the electrodes, multiple degrees of freedom in movement can be achieved in these actuators and bending motions along with elongations have been reported. Lateral forces of up to 1.5 N have been noted in cylindrical devices as the actuator bends.

Stacked actuators\textsuperscript{49} (Figure 2.34) consist of thousands of DE films piled together with compliant electrodes sandwiched in between these films. To facilitate easy fabrication helical and folded designs are used. In helical form\textsuperscript{49} (Figure 2.34), only two continuous electrodes are used and the actuator generated compressive strains of about 5\% at 14 V/\mu m. In the folded configuration (Figure 2.35), the continuous electrodes are folded such that two electrodes stay opposite to each other. Compressive stresses and strains of about 6 kPa were generated. Arora et al.\textsuperscript{50} and Cameron et al.\textsuperscript{51} have also proposed tubular configurations. Arora and coworkers used silicone and polyurethane tubes and applied prestrain by uniaxial
elongation and inflation. The actuators generated axial strain of 7% (Figure 2.36a). Cameron et al. coextruded DE tubes consisting of conductive cores of graphite reinforced poly(dimethylsiloxane) and shells of elastomeric polyurethane. The extrusion process can be scaled up easily to mass produce small diameter tubes or hollow fibers. The actuators (Figure 2.36b) thus made from these tubes showed axial strains of ~ 2%.

The BCDEs have not been so far explored for making into these configurations. They are extremely viable materials to be molded into any of these configurations due to their thermoplastic nature that offer facile processing. Customization into a variety of shapes/forms is a real possibility with techniques such as injection molding. BCDEs offer the flexibility, unlike conventional homopolymeric chemically crosslinked DEs, of subsequent remolding in case of pronounced defects and deformities occurring during processing. This allows, for example, having different kinds of cross-sections in folded configurations. The shape customization is important for DE applications in loudspeaker films (Figure 2.37) where speaker shapes can affect both sound pressure level and the directivity. The films need to charge and discharge at acoustic frequencies and hence demand tunability in this aspect. Response time and hence the frequencies of BC-based elastomers can be tuned as was demonstrated in blends of SEBS/MO with tackifying resins. These elastomers are lightweight, scalable to small and large areas, and conform well to flat and nonflat surfaces when used as loudspeakers. The electric field required for these elastomers to actuate can be tuned by varying the copolymer/ MO composition and can be as low as ~ 20 V/μm with achievable areal actuations of about 250% with prestrain as seen for SEBS/MO blends. These values in combination with the quick response of the blends can be used for diffraction
gratings where the required strains are about 27%. Aschwanden and Stemmer have fabricated a diffraction grating using an acrylic VHB elastomer, prestrained and printed with electrodes, and PDMS grating pattern cured to the elastomer (Figure 2.38).\textsuperscript{53} The VHB elastomer and PDMS both could potentially be replaced by SEBS/MO system. With addition of tackifying resins to this system the modulus values of these materials (currently reported at 190 kPa) can be raised to 280 kPa to suit this application. The SEBS blends also demonstrate less than 18\% hysteresis (under the tested conditions) and could suit the required frequency of 50Hz.

As noted before, prestrain requires additional frames to support the DE adding to the weight of the device. The DE film could relax over time at the frame boundaries and eventually fail. The most applicable DE configuration is the spring roll and folded, where prestrain is applied to the film. DEs based on acrylic block copolymers that require no prestrain could be fabricated into these configurations and used in robotics essentially eliminating the challenges that come with prestrain. The availability of these DEs also opens doors for their utility in limbs and prosthetics. Currently, no DE meets the life-cycle expectancy of these limbs. Though the BCDEs are not evaluated for this performance, they are quite attractive in reducing the present actuator weight by about 98\% existing mainly due to prestrain supporting frames and packaging in limb prosthetics.\textsuperscript{54} The BCDEs also actuate at much lower fields than the conventional DEs (actuating at \~100 V/\mu m) and, additionally, cut down on the limb weight by facilitating use of small and compact power supplies. For prosthetic applications viscoelasticity of DEs is also important as it manifests into stiffness changes with varying strain rates and frequencies. With the addition of solvent and co-solvent, such as tackifying resins, into the broad spectrum of network-forming block
copolymers, the viscoelastic behavior can be very well be tuned making the material more reliable. This also reduces the hysteretic losses during repetitive cycling and increases the energy efficiency of the actuators. The BCDEs can also be molded into tubes and used as tube-actuators for making refreshable Braille displays. Recently, silicone tubes have been reported for this application\(^5\)\(\text{cf. Figure 2.39}\) that demands the axial strains of 0.5 mm and blocking force of 0.3 N. With the versatility in (electro)mechanical properties offered by BC systems, achieving these values would not be very difficult.

Other areas where DEs can find applicability include energy harvesting\(^6\) and telecommunications.\(^7\) When a prestretched and precharged elastomer holding a fixed amount of charge on the electrodes (open-circuit condition) thickens in one dimension due to reduced tensile force on it, the voltage increases causing electric charge to flow from low-voltage source to high voltage reservoir that can store energy (Figure 2.40).\(^8\) Existing DEs used for this purpose are prestrained up to 100%, excited with a frequency of under 1Hz thus converting energy just below 0.1 J/g. As the prestrain is increased the conversion effectively increases by a few orders of magnitude. Other properties of DEs such as modulus, dielectric constant, dielectric strength are also critical. High modulus reduces the electromechanical instability by reducing the wrinkling effect and increases the conversion. As dielectric constant and strength increases, the achievable Maxwell stress increases that effectively improve the conversion. Typically, natural rubber and VHB acrylic have been tested for this purpose, which being chemically crosslinked cannot be reprocessed once formed into a particular geometry. DE of modulus of about 1 MPa and Maxwell stress of about 10 MPa are reported so far for this application. The BC-based systems (with/without tackifying resins)
are capable of offering the mentioned required properties along with the possibility of shape/size customization facilitated by their thermally reprocessable nature of physical (and not chemical) crosslinks. Facile thermal processing facilitates the construction energy harvesting devices in all sizes ranging from miniature to large scale versions. The breakdown field of BCDEs can be tuned by an appropriate choice of blend composition in a given BC system. Though biaxial prestrains above 300% remain to be tested, potentially they could be higher than 100%, thus increasing the energy conversion while in operation, as the materials in most cases do not fail until beyond 2000% strain in uniaxial tensile testing. In all, the BC systems are more flexible for this application as their properties can be varied to suit the requirements by varying the blend composition which can be then easily processed and fabricated.

The single-mode optical fiber is a commonly used optical component in telecommunications packages. The alignment of these fibers to sources is extremely challenging with tolerance values in a few microns. A lateral misalignment of these fibers, for example, by 3 μm can drop the transmission by 3 dB. Traditionally, specialist robotic techniques have been used for this purpose that demand huge initial costs. In another approach, microelectromechanical systems (MEMS) are also studied, but lack attraction due to high productions cost, poor reliability due to their complex delicate structure, high operating voltages and large energy dissipations. The EAPs are seen to offer a solution as they are cheap, easy to construct into a device, have simple structures, are lightweight and low maintenance. The properties requirements of DEs of high dielectric constant, low modulus and thinner films for this application can be met by an appropriate choice of a BC
networked blends. When VHB is used for this application, prestrained in a square frame and containing an optical fiber mounting disc at the center as mentioned by Jordan et al. (Figure 2.41), it suffers from viscoelastic losses and creep resulting into hysteresis that is not desirable as the design can lose its alignment accuracy, thus, necessitating the need for feedback control loops that can account for these effects. As the amount of oil in BC blends is varied the viscoelastic losses and hysteresis can be minimized, reaching almost to none. The modulus can be as low as 5 kPa for SEBS/MO system depending on the copolymer molecular weight and the composition.

Similar to DEs, IPMCs find wide applications as transducers, actuators, sensors and artificial muscles. Here we consider some of the application where the BCIPMCs could potentially be used and would like to point out that the list of application is not limited to the ones enumerated below. The BCIPMCs can be tuned for their stiffness by varying the amount of solvent which can be varied in turn by varying the sulfonation level in the copolymer. Materials with different stiffness would allow tuning of force that the IPMC would generate. These features will help in use of these materials into design of mechanical devices such as grippers (Figure 2.42) that can handle materials of different softness and metering valves and diaphragm pumps that can control materials flow in pipes. Grippers are designed with two IPMC strips clamped at one end and electrodes wired such they move in opposite direction under the applied voltage. The BCIPMCs demonstrate reversibility in bending direction when the polarity of electrodes is switched thus making them a good candidate for gripper applications. These grippers in the form of fingers can be mounted on robotic arms that can be used to sample planetary rocks with ultra-dexterity and versatile
handleability. The IPMCs can be installed inside pipes as metering valves with one end secured to the pipe and the other floating into the liquid flowing. By controlling the bending of the IPMC the flow could be regulated. Tunability in force that the IPMCs can generate is a key property that still needs to be tested for the BCIPMCs for this application. As BC can be fabricated conveniently into any shapes, the IPMCs made from these geometries can also be made into diaphragms and used in designing noise-free single or double diaphragm mini/micro pumps capable of controlling flow in the range of few microliters/min. An application of these pumps is as ocular pressure control devices. They are implanted in conjunction with eye conduits to pump in (out) drugs (drainage fluids).

An interesting fluid propulsion/mass transfer system was recently demonstrated by Sareh et al.\(^6\) comprising of Nafion\(^\circledast\)-based IPMCs that mimicked whip-like appendages or microscopic cell organelles such as flagella and cilia that many living cells use to propel themselves or move fluids. Typically, cilia have dimensions of 1 μm to 2 mm and actuate at about 20-30 Hz. The IPMC features of low voltage activation, zero-noise operation, scalability and multiple degrees of freedom make them attractive to be made into these structures. For fluid propulsion/mass transfer, an IPMC should be capable of generating a wave-like (undulating) motion. The electrodes can be patterned on the IPMC to create a wave when subjected to an appropriate input signal that can create a directional, either longitudinal or lateral, propulsion/fluid flow. Sareh and coworkers used a two segment IPMC design as shown in Figure 2.43. The segments were subjected to voltage sine waves that had a phase difference. The result was the undulatory IPMC motion that closely mimicked cilia motion. The wave motion in the IPMC could be controlled to generate both,
turbulent (Figure 2.43) and extremely well-directed, flows. The BCIPMCs show reversibility in bending direction when the voltage polarities are interchanged under DC field and hence can potentially form wave motions. The electrodes can be patterned easily and the resultant IPMCs can possible be used for propulsion/fluid transport in robotic and bio-mimetic devices. A variety of symmetric and asymmetric fluid flows patterns can be generated using IPMCs.

The IPMCs, due to their softness and flexibility, can also be used in a number of biomedical applications. If the IPMC solvent is biocompatible, the IPMCs can potentially be used as artificial ventricular assist-muscles that engulf the heart from outside and are partly sutured to heart without contacting or interfering with blood vessels thus avoiding complications such as thrombosis resulting from repetitive contact of a foreign implant with the circulating blood. The muscles help in heart contractions to regulate the blood flow by squeezing the left ventricle in harmony with the systolic ventricular contractions. Besides this application, the IPMCs can prove to be imperative in surgeries when used as active guide-wire in cardiac catheterization, a common procedure to diagnose/treat cardiac diseases.\textsuperscript{61} Active guide-wire or catheter systems have been a focus of study as they can eliminate the inconvenience of changing guidewires during surgery to pass bifurcated blood vessels. The IPMCs mounted on catheter/guide-wire tips can help tune the curvature of the device in the vessels (Figure 2.44). A large deformation at low frequencies has been shown to be effective for this purpose. The BCIPMCs show extensive deformation at DC potential that are quite close to AC frequencies of 0.01 Hz and can be used as catheter tips. When IPMCs are used for this purpose, feedback control loops are used to precisely control the tip position by
accounting for non-linear effects involved with IPMC actuation such as hysteresis and back-relaxation. The input feedback signals to the control loops are currently measured by sensors such as laser displacement devices, CCD cameras etc. that make the system bulky and hence restricted in applicability. The IPMCs can itself function as a sensor by generating voltage signals on deformation that can be used to accurately position the tip. The current research interests are in this area of utilizing IPMCs both, as actuator to guide the catheter into blood vessels and as sensor to precisely position the tip for control on direction. The IPMCs can be packaged into designs to augment the power and mobility of skeletal muscles. These designs integrate IPMCs into systems that are in the form or exoskeletal prosthetics, orthosis, wearable muscle fabrics components such as jackets, trousers, boots etc. For example, an elbow joint made in a prosthetic arm by a set of IPMCs can enhance and control arm mobility. Besides these applications, IPMCs can also be tailored for use as artificial sphincters and ocular muscles.

Similar to DEs, IPMCs can be employed as energy harvesters.\textsuperscript{62, 63} An IPMC actuator is subjected to sinusoidal vibrational motion by a shaker and the resultant IPMC movement generates a sinusoidal voltage signal that is converted into DC signal by a full-wave rectifier and then stored on a large capacitor and can be used to charge a battery. A disc shaped IPMC can also be used for this purpose. Tiwari and Kim\textsuperscript{64} demonstrated this concept by melt pressing Naion\textsuperscript{®} pellets into a disc and using a configuration as shown in Figure 2.45. A disc shaped IPMC offers the advantage of harvesting energy from uncontrolled multi-dimensional vibrations along multiple IPMC dimensions, for example, along the disc height using E1 set of electrodes and along thickness via E2 electrodes (\textit{cf.} Figure 2.45). Disc shaped IPMCs
showed that vibrational motion induced from a mechanical shaker generated stresses, mainly along the radial direction, that can be converted to energy. The energy generated was up to 2 times in an hour than that noted for bender-type IPMC energy harvester. The energy harvested was a function of dimensions and increased as height and/or thickness of the IPMC increase. The BC-based ionomers can be customized into any shapes easily by solvent casting and the stiffness can be controlled by controlling the solvent uptake, which in turn can be controlled easily by varying sulfonic acid content. The Nafion® films lack this stiffness that may be required for energy harvesting in certain applications.  

The BCIPMCs due to their tunable mechanical and electromechanical response certainly form new and interesting materials to explore for these applications. They can also find utility in some other applications, where conventional IPMCs have been reported to find applicability. They can likely be used as a vibration sensing transducer due to the inherent capability of IPMCs to generate an electric voltage signal when deformed. Tactile sensor is another area where these new IPMCs can find use. As shown by Bonomo and coworkers, IPMC when actuated can vibrate and contact the tissues thus measuring their stiffness and hence identifying their type. Additionally, the IPMCs can be explored for blood pressure, pulse rate and rhythm measurement devices and as pressure transducers for the human spine.
2.5 Conclusions

Electroactive polymers (EAPs) fall in the category of stimulus-responsive materials that require an electrical input to generate a mechanical deformation. This deformation can be used to perform work. Block copolymers (BCs), used widely in applications such as adhesives, vibration-dampening and shape memory, have been recently reported as dielectric elastomers (DEs) and ionic polymer metal composites (IPMCs)—two subclasses of EAPs. While DEs can be used in a variety of applications ranging from robotics to energy harvesting, IPMCs can find applications in mini/micro robotics, as mechanical devices, artificial muscles, prosthetics, surgical aids and motion sensors. The BC-based systems used as these EAPs consist of microphase separated physically networked morphologies, where the phase separated domains can be selectively swollen by high boiling solvent. With the introduction of these materials several existing hurdles reported for DEs and IPMCs are resolved. In the case of DEs, triblock copolymers having styrenic endblocks and aliphatic midblock selectively solvated with mineral oil showed robust mechanical properties (tunable modulus, low hysteresis and high failure strains) and tunable actuation performance. The response time of these DEs can be controllable varied by including co-solvents such as tackifying resins making them suitable for applications like time switches. The design was extended to an all-acrylic block copolymer system, which showed extensive actuation strains with no need for mechanical prestrain that is usually required for DE actuations, thus, nullifying the need for bulky frames to hold the prestrain in a device that reduces its work density. The electromechanical properties of BCDEs can broadly be tuned by variation in copolymer parameters (i.e., molecular weight, block sizes, chemistry, copolymer
concentration in a gel) and/or the solvent quality. The concept of using networked BCs for DEs can be further extended to IPMCs. Multi-block copolymer having microphase separated network with one of the blocks ionic in nature formed a high-performance IPMC and eliminated some concerns seen with conventional IPMCs, such as shape customization during fabrication and back-relaxation during actuation. The possibility to tune properties of these BC-based materials opens doors for several applications. Some applications that could be explored for BCDEs include loudspeaker diaphragms, pumps, diffraction gratings, prosthetics, energy harvesting and telecommunications. The BCIPMCs could be used to make mechanical devices such as grippers, metering valves, propulsion systems, artificial muscles, catheters, and energy generation devices. To fully explore these and many more applications additional research that characterizes the material properties (such as force generation by DEs and IPMCs) and evaluates performance (for example, cyclic performance over several thousand cycles) needs to be done. However, considering the available knowledge of these materials and the immense potential they have demonstrated so far in terms of performance, they certainly form interesting materials that researchers will be willing to explore.
Figure 2.1 Morphologies seen in AB or ABA block copolymer as a function of block fraction. S, C, G, L stands for spherical, cylindrical, bycontinuous (gyroid) and lamellar morphologies respectively.⁴
Figure 2.2 Phase behavior of Poly(isoprene-b-styrene-b-ethylene oxide) (ISO) terblock copolymer.\textsuperscript{5}
Figure 2.3 Dielectric constants as a function of copolymer composition for ENP161 (filled circles) and ENP217 series (open circles). For comparison purposes values for silicones and acrylics are provided.\textsuperscript{8}
Figure 2.4 Tensile modulus as a function of copolymer concentration for ENP75 (diamonds), ENP161 (triangles) and ENP217 (circles) series. Comparison with acrylics is shown as a dotted line.\textsuperscript{8}
Figure 2.5 Maximum actuation ($s_{act}$) and transverse strains $|s_z|$ as a function of copolymer concentration for ENP161 (triangles) and ENP217 (circles) series. Comparison with silicones and acrylies is also shown.\textsuperscript{8}
Figure 2.6 (a) Dielectric breakdown as a function of copolymer concentration is shown for ENP161 (triangles) and ENP217 (circles) series. Shaded region and dotted lines indicated values for silicones and acrylics, respectively. (b) Maximum actuation ($s_{act}$) in terms of dielectric breakdown is shown. Comparison with silicones (+) and acrylic (X) is included.\(^8\)
Figure 2.7 (a) Solid circles indicate the areal actuation achieved by networked system of ENP75 containing 70 wt% oil under no mechanical prestrain. The dashed lines are actuation data for acrylics labeled as two different grades of VHB tested tested under similar conditions. (b) Energy density of the material described in (a) compared to acrylic VHB.\textsuperscript{12}
Figure 2.8 Time-dependent actuation behavior of DEs made of SEBS solvated with 70 wt% MO, tackifying resin or their mixtures when subjected to voltage jumps to one of the electric two indicated in a color-code.¹³
Figure 2.9 Area actuation of SEBS/MO DEs obtained by biaxially prestraining films of thicknesses of (a) 1.8 mm and (b) 3.0 mm to 300%. Films had different compositions (in wt%): 5 (filled diamonds), 10 (open circles), 15 (filled circles), 20 (open triangles), 25 (filled triangles) and 30 (open diamonds).\textsuperscript{14}
Figure 2.10 Maxwell stress- transverse strain curves for SEBS?MO films of thickness 1.8 mm biaxially prestrained to (a) 100, (b) 200 and (c) 300 %. Different film compositions in
terms of copolymer concentrations (in wt%): 5 (filled diamonds), 10 (open circles), 15 (filled circles), 20 (open triangles), 25 (filled triangles) and 30 (open diamonds).

Figure 2.11 Maxwell stress for all the curves for SEBS/MO systems shown in Figure 10 is normalized by respective electromechanical modulus and a master curve is obtained. The symbols match with those in Figure 10.
Figure 2.12 Electromechanical stress strain curves for a SEBS/MO gel of 25 wt% copolymer concentration made into films of different thicknesses: 0.5 mm (filled circles), 1.0 (open
circles), 1.8 (filled triangles) and 3.0 mm (open triangles) prestrained to (a) 100, (b) 200 and (c) 300% prestrains.\(^{14}\)

Figure 2.13 Dielectric breakdown of DEs made from SEBS/MO having (a) 10 and (b) 30 wt\% copolymers as a function of prestrain for specimens with different initial thicknesses (in mm): 0.5 mm (filled circles), 1.0 (open circles), 1.8 (filled triangles) and 3.0 mm (open triangles).\(^{14}\)
Figure 2.14 Dielectric breakdown of SEBS/MO-based DEs biaxially prestrained to 300% and having different copolymer concentrations: 5 (filled diamonds), 10 (open circles), 15 (filled circles), 20 (open triangles), 25 (filled triangles) and 30 (open diamonds). \(^{14}\)
Figure 2.15 Actuation strains measured for composites of coated TiO$_2$ at 100% prestrain
Inset shows the dielectric spectra of these composites. The permittivity can be seen to
increase as the particle concentration increased.$^{17}$
Figure 2.16 Effect on breakdown strength (field) and energy density as TIO$_2$ concentration increased.$^{17}$
Figure 2.17 (a) and (b) Dielectric spectra of PANI-grafted SEBS-MA copolymer. In the top plot two regions are seen. At low grafting percentages, permittivity and conductivities both stay flat with frequency. In the second region, both become frequency dependent and increase by an order of magnitude.\textsuperscript{17}
Figure 2.18 Electrical breakdown fields and corresponding energy densities and actuation strains for PANI-grafted SEBS-MA series.\textsuperscript{17}
Figure 2.19 (a) Maximum actuation strain for two all-acrylic block copolymer (MBM) series.
(b) Electromechanical $\varphi$-$\lambda$ (potential-stretch) lines as suggested by Zhao and Suo.\textsuperscript{13}
Figure 2.20 Schematic of an IPMC.

Figure 2.21 Chemical structure of endblock sulfonated poly[styrene-\(b\)-(ethylene-\(co\)-butylene)-\(b\)-styrene)] (SSEBS).\(^{41}\)
Figure 2.22 (a) Surface and (b) cross-sectional images of SSEBS-based IPMC taken with SEM. \(^\text{41}\)

Figure 2.23 Tip displacement of SSEBS-based IPMCs subjected to different DC voltages. \(^\text{41}\)
Figure 2.24 Tip displacement of SSEBS-based IPMC under AC signal of 0.2 Hz and amplitude of 1.5 V.$^{41}$
Figure 2.25 Electrode surface image of the IPMC made from CNF-SSEBS composite.\textsuperscript{42}

Figure 2.26 Cross-sectional image showing the uniform distribution of CNF in SSEBS matrix.\textsuperscript{42}
Figure 2.27 Single CNF imaged by SEM in SSEBS matrix.\textsuperscript{42}

Figure 2.28 Tip deflection of IPMC derived from CNF-SSEBS under DC voltage compared to the one made from neat SSEBS.\textsuperscript{42}
Figure 2.29 Mean deflection responses for CNF-SSEBS IPMCs under AC voltages.\textsuperscript{42}

Figure 2.30 Schematic illustration of the micellar morphology in a midblock-sulfonated tbSEP sbSEP sbS block ionomer.
Figure 2.31 Comparisons for IPMCs made from tbSEPsSEPtbS, Nafion® and SSEBS with water as solvent when subjected to DC potential. In all cases, deflection of the IPMC was towards anode.
Figure 2.32 (a) Actuation as a function of time for tbSEPsSEPtbS-based IPMCs prepared with glycerol as solvent (filled symbols, solid lines, labeled with the cation and applied voltage) and IPMCs based on Nafion® reported elsewhere (open symbols, dotted lines, labeled with the cation, at 2 V). (b) Superimposed snapshots of the actuation achieved at 7V as time progresses.13
Figure 2.33 Fabrication process of a DE spring-roll actuator configuration.⁴⁸
Figure 2.34 (a) Stacked and (b) helical configurations of DE actuator.\textsuperscript{49}
Figure 2.35 Fabrication and assembly of folded configuration of a DE actuator.
Figure 2.36 (a) Prototype of uniaxially strained fiber actuator set-up. (b) Rope actuator capped on ends by epoxy.

Figure 2.37 Loudspeaker film in (a) convex and (b) flat shapes made from DE.
Figure 2.38 Schematic for step-by-step fabrication process for DE-based diffraction grating. (a) DE actuator is assembled, (b) Elastomer is spin-coated onto mater grating, (c) Elatomer bonded to DE actuator, (d) mater grating removed and (e) Gold layer evaporated on diffraction grating to enhance reflection.\textsuperscript{53}
Figure 2.39 Schematic for the design of Braille cell made from tubular silicone DE.\textsuperscript{55}
Figure 2.40 Schematic of energy harvesting protocol using a DE: 1) DE is deformed, 2) charged, 3) DE relaxed and 4) charge harvested.\textsuperscript{58}

Figure 2.41 (a) A DE is prestrained between two frames. Electrodes are applied on bottom half on two sides of the film. At the center of the film is a circular disc where the optical fiber to be positioned can be mounted. As the bottom half is actuated the lateral movement of the
active area results in vertical movement of the fiber that then can be positioned accurately.

(b) Two degree of freedom (2-DOF) DE submount. Each active area (shown in dark) can be driven independently to position the fiber.⁵⁷

Figure 2.42 A gripper concept using IPMC.⁵⁹

Figure 2.43 A two segment IPMC used to mimic cilia-type motion to propel fluid. On the left, an example of a two-segmented IPMC producing and unsteady flow is shown.⁶⁰
Figure 2.44 On the left: a sketch of how a guide-wire is used in cardiac catheterization. On the right: A- traditional guide-wire, Active guide wire with IPMC tip.61
Figure 2.45 (a) Shows a disc-shaped IPMC with electrodes to harness energy along two directions— height and thickness. (b) Shows the actual setup used to collect the energy. 

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2.6 References

(1) Brochu, P. and Pei, Q. B. *Macromolecular Rapid Communications*, 31 (2010), 10.


(10) Krishnan, A., S. *et al.* *Langmuir*, (submitted),


Kim, K. J. and Shahinpoor, M. *Smart Materials & Structures*, **12** (2003), 65.


Bennett, M. D. and Leo, D. J. *Sensors and Actuators a-Physical*, **115** (2004), 79.


(55) Chakraborti, P. M.S. Thesis: *Development of a refreshable braille display using silicone tubular dielectric elastomer actuators (DEA)*, North Carolina State University, NC, USA (2010), 118.


(64) Tiwari, R. and Kim, K. J. *Smart Materials & Structures*, **19** (2010), 065016.


3 (Electro)Mechanical Behavior of Ternary Thermoplastic Elastomer Gels

Physically cross-linked thermoplastic elastomer gels (TPEGs) composed of ABA-type triblock copolymers with selectively solvated midblocks continue to gain considerable scientific and technological interest.\textsuperscript{1-4} In the presence of a B-selective solvent, the incompatible endblocks seek to reduce the number of repulsive contacts and thus self-organize to form microdomain cores surrounded by a shell of swollen B midblocks.\textsuperscript{5} In most cases, the microdomains can be described as discrete spherical micelles that can, depending on copolymer concentration, be arranged on a cubic lattice. Moreover, the copolymer concentration is above the critical gel concentration at which the micelles become physically connected by bridged midblocks. Since the copolymer is a thermoplastic elastomer consisting of glassy or semicrystalline endblocks and a rubbery midblock, the micelles, which are glassy at ambient temperature, serve as physical cross-link sites that stabilize the accompanying network of swollen midblocks. Under these conditions, the resultant TPEG exhibit desirable mechanical properties, such as remarkable elasticity and extension to break.\textsuperscript{6} These properties depend sensitively on the fraction of midblocks that are bridged and, therefore, on the copolymer concentration.\textsuperscript{7} This fraction can alternatively be changed at constant copolymer concentration through the addition of "matched" diblock copolymer molecules (possessing the same chemistry and composition, but half the molecular weight).\textsuperscript{8} Previous rheological studies of TPEGs containing a mixture of both diblock and triblock copolymers have demonstrated that the bridged midblock fraction can be increased, as
evidenced by an increase in the dynamic storage modulus, upon small additions of diblock copolymer at constant copolymer concentration. Common TPEGs incorporate ABA triblock copolymers composed of polystyrene endblocks and a polydiene or polyolefin midblock and a low-volatility, aliphatic solvent. Recent efforts have likewise established that the design paradigm responsible for styrenic TPEGs is general and can be readily extended to other copolymers, such as acrylic thermoplastic elastomers, with appropriate midblock-selective solvents. These soft, elastic materials have been ubiquitously used in a wide variety of (nano)technologies ranging from pressure-sensitive adhesives and vibration-dampening media to consumer and sporting goods and microfluidic substrates. An exciting and relatively new application of TPEGs is as electroactive polymers (EAPs). This broad class of stimuli-responsive polymers can be divided into several different categories on the basis of the mechanism by which they undergo actuation upon exposure to an externally applied electric potential. Of all the categories identified thus far, dielectric elastomers (DEs), or electroelastomers, show the most promise as soft materials that are capable of exhibiting giant actuation strains with surprisingly little hysteresis upon strain cycling. Although they typically require relatively large electric fields to actuate, they can be remarkably tunable and designed from the ground up to possess properties that emulate, for example, mammalian skeletal muscle. In addition to serving as synthetic muscle, these EAPs have drawn considerable attention for use in technologies ranging from micro air vehicles and microrobotics to flat panel speakers and refreshable Braille tablets. They are particularly attractive for several reasons: low cost, light weight, facile processability, low hysteresis and mechanical robustness.
In the same spirit as their inorganic counterparts (e.g., shape-memory alloys\textsuperscript{14} and piezoelectric ceramics\textsuperscript{15}), EAPs are of general commercial and fundamental interest because they convert electrical energy into mechanical work by changing size and/or shape during actuation. Specifically, DEs undergo actuation due to electrostatic attraction between oppositely charged compliant electrodes, which introduce a Maxwell stress that compresses the DE transversely (along the thickness direction).\textsuperscript{16} Since this deformation is isochoric, the DE expands laterally (in-plane). The actuation strain, presented on an area basis, is measured as the change in the active (electrode) area relative to the initial area prior to actuation. Material stiffness dictated by the modulus largely controls the electric field required to actuate a DE, while extensibility affects the maximum actuation strain that can be achieved. If the midblocks in a TPEG are short and marginally swellable, the modulus is high and the maximum actuation strain is expectedly small. If the midblocks are long and highly swellable, the modulus is low, but the actuation strain can be huge (approaching 300\%).\textsuperscript{6} For design purposes, it is desirable to tune the modulus and extensibility independently. In this work, we demonstrate that this can be achieved in TPEGs by employing blends of diblock and triblock copolymers in the presence of a midblock-selective solvent. By adding a "matched" diblock, the fraction of midblock bridges stabilizing the swollen midblock network can be controllably adjusted. At a fixed copolymer concentration, the effective cross-link density derived from the population of glassy micelles is expected to remain unchanged as mixed micelles develop. As the concentration of diblock copolymer is increased, diblock molecules replace triblock copolymers and reduce the fraction of bridged midblocks, as well as the network integrity needed to ensure full recoverability of the DE.
after actuation. The objective of the present study is to examine the (electro)mechanical properties of ternary TPEGs and discern whether these properties can be controllably adjusted by altering composition.

The two commercial copolymers employed here were a poly[styrene-\(b\)-(ethylene-co-propylene)] (SEP) diblock copolymer and a poly[styrene-\(b\)-(ethylene-co-propylene)-\(b\)-styrene] (SEPS) triblock copolymer, both provided by Kuraray America Ltd. (Houston, TX). According to the manufacturer, the composition and number-average molecular weight of the triblock copolymer were ~35 wt% S and 305 kDa, respectively, whereas those of the diblock copolymer were ~36 wt% S and 150 kDa, respectively. The midblock-selective solvent mixed with the copolymers was an aliphatic/acyclic white mineral oil (MO, Hydrobrite 380; Sonneborn, Inc., Tarrytown, NY) with a molecular weight of ~500 Da. Reagent-grade toluene was obtained from Fisher Scientific (USA) and used as-received. The ternary TPEGs investigated here were prepared by solution blending one or both copolymers with MO in toluene to produce solutions containing 5 wt% polymer. Slow evaporation of the toluene over the course of 3 days yielded films measuring ~1 mm thick. These resultant films were annealed at 160°C under vacuum for 12 h to remove residual solvent and promote nanostructural refinement, and subsequently hot-pressed at 160°C to ensure uniform specimen thickness of 0.7 mm. Quasi-static and cyclic nominal stress-stretch measurements were conducted on a MTS-30G load frame operated at a constant crosshead speed of 127 mm/min at ambient temperature. The actuation response of the films to an electric field was investigated in the conventional circular test configuration. Specimens were first subjected to 300% equibiaxial prestrain on a rigid frame to decrease film thickness and thus increase the
magnitude of the electric field at manageable electric potentials. Compliant electrodes (Ag silicone grease from Chemtronics Circuit Works, Kennesaw, GA), applied as the circular active area to the top and bottom surfaces of each film, were connected to a Bertan 225-30R high-voltage power supply (Spellman High Voltage Electronics Corp., Hauppauge, NY). Electroactuation of select films was induced by an automated voltage trigger, which ramped the potential at 250 V/s while the in-plane expansion of the active area was digitally recorded. Resulting footage was analyzed frame-by-frame with the MATROX® Inspector 4.0 software package to determine the corresponding actuation strain as a function of electric field.

The composition of the ternary TPEGs investigated here relies on two independent measures: (i) the total concentration of copolymer (SEP + SEPS) present (denoted $\phi$ and expressed in terms of wt% of the TPEG), and (ii) the concentration of SEP diblock copolymer (denoted $\psi$ and expressed in terms of wt% of the total copolymer concentration). These two composition metrics are not, however, completely independent, since the range of testable specimens depends on both compositions. This range is fixed at one end by the mechanical integrity of the films, which governs the extent to which the films can be handled and measured without inducing premature damage. The other end of this range is dictated by the melt processability of the films. When $\phi$ is relatively low ($\leq 30$ wt%), films without the diblock copolymer can be readily processed into uniform sheets. Holding $\phi$ constant at 30 wt% and increasing $\psi$ results in weakened TPEGs as 2 diblock molecules replace each triblock molecule and the connectivity of the swollen midblock network is effectively diminished, as illustrated in Fig. 3.1. These materials become unmanageably tacky and
difficult to melt-press into testable films when \( \psi \) is increased beyond 50 wt\%. We therefore assign these conditions as a composition boundary. Similarly, when \( \phi = 10 \) wt\%, \( \psi \) could only be increased up to 20 wt\%, which extends the composition boundary identified above for weak TPEGs.

At copolymer concentrations above 30 wt\%, the TPEGs possess high tensile moduli, as determined from their stress-stretch curves and presented in Fig. 3.2. While excessively high moduli eliminate the suitability of these TPEGs for our present electroactuation purposes, such materials are certainly beneficial in other applications. In addition, this limit can be shifted to higher values of \( \phi \) by using block copolymers with a lower styrenic content. Increased stiffness in this limit is generally attributed to a reduction in the concentration of MO, which is responsible for swelling the midblocks (and, to a much lesser extent, the endblocks) of TPEGs, and concurrently increasing the concentration of glassy styrenic endblocks. In this limit, TPEGs with \( \psi \) below a \( \phi \)-dependent concentration could not be melt-pressed into smooth films without causing material degradation due to their high melt viscosities. Thus, on the basis of melt processability, we establish a second composition boundary at copolymer concentrations in excess of 50 wt\% due to the unacceptably high moduli and associated processability limitations. In light of these experimental boundaries, we specifically turn our attention to the following TPEG compositions: (i) \( \phi = 30 \) wt\% and \( \psi \leq 50 \) wt\% and (ii) \( \phi = 10 \) wt\% and \( \psi \leq 20 \) wt\%.

The objective of blending diblock and triblock copolymers in TPEGs is to controllably alter the fraction of bridged midblocks responsible for network integrity. Although experimental methods are available to discern this quantity directly, they are not applicable in
this study. Rather, an indirect measure of network connectivity can be deduced by fitting the slip-tube network (STN) model proposed by Rubinstein and Panyukov\textsuperscript{17} to nominal stress-stretch ($\sigma$–$\lambda$) data acquired at different concentrations of total copolymer and diblock copolymer. Here, the stretch, or extension ratio, is defined as 1+$\varepsilon$, where $\varepsilon$ denotes tensile strain. This hyperelastic model can be written as

$$\sigma = \left( G_b + \frac{G_e}{h(\lambda)} \right) \left( \frac{\lambda - 1}{\lambda^2} \right) f(\Omega, \Theta)$$

where $G_b$ and $G_e$ represent contributions to the shear modulus (G) due to bridged midblock (physical cross-links in this case) and transient entanglements, respectively. The function $h(\lambda)$ is given by $0.74\lambda + 0.61\lambda^{-1/2} - 0.35$, and $f(\Omega, \Theta)$ depends on both copolymer volume fraction ($\Omega$) and filler concentration ($\Theta$) for a TPEG composed of swollen rubbery matrix and a dispersed solid filler. The value of $\Theta$ refers to the styrenic content of the copolymers and is fixed for the systems under investigation, whereas $\Omega \approx \phi$, which is set equal to 10 or 30 wt% and is constant within each series. Thus, within a given TPEG series of constant copolymer concentration, $f(\Omega, \Theta)$ effectively becomes a constant and can be represented as simply $f$. Note that, at small tensile deformations, $\lambda \to 1$, in which case $G_b + G_e$ is equivalent to G. At large deformations, the material stiffness depends only on $G_b$, i.e., the contribution from bridged midblocks.

Regressions of Eq. 1 to the data collected from the TPEGs of interest here are displayed in Fig. 3.3. The figure reveals several trends in tensile behavior as $\psi$ is varied. First, while the $\sigma$–$\lambda$ curves in all cases are nonlinear, those acquired from TPEGs with $\phi = 30$ wt% show
the most deviation from linearity. At $\phi = 10$ wt% in Fig. 3.3a, there is surprisingly little difference in the stress response of the TPEGs as $\psi$ is increased from 0 to 20 wt%. When $\phi = 30$ wt% (cf. Fig. 3.3b), however, the $\sigma-\lambda$ curves shift noticeably to lower stress as $\psi$ is increased from 0 to 50 wt%, and the TPEGs show increasing evidence of strain softening at intermediate deformation ($2 < \lambda < 6$). At larger deformation, strain hardening becomes apparent (data not shown). That is, at a given stress, the corresponding strain values become increasingly different as $\psi$ increases. The onset of strain hardening occurs at larger values of $\lambda$ with increasing diblock concentration. Regression analysis of the STN model appears accurate up to $\lambda = 6$, beyond which it fails to describe the strain hardening regime, since this phenomenon is not incorporated into the model. While the $\sigma-\lambda$ data acquired here can also be analyzed in terms of other, often empirical, hyperelastic models, the STN formalism captures strain softening well and provides parameters that afford valuable insight into the swollen midblock network.\(^8\) Since, for instance, $G_b$ dominates at large strains, the occurrence of strain softening can be attributed largely a reduction in the population of bridged midblocks, which agrees with intuitive expectation as an increasing number of SEP molecules replace SEPS molecules (which are needed to form bridges) as $\psi$ is increased.

The relative contributions from midblock bridges and transient entanglements in the TPEGs with $\phi = 30$ wt% can be evaluated by considering the STN parameters $G_bf$ and $G_ef$ extracted from the regressions in Fig. 3.3 and displayed as a function of $\psi$ in Fig. 3.4. The results provided in this figure reveal two important features. The first is that $G_bf$ is, for the most part, larger in magnitude than $G_ef$ over the range of $\psi$ examined, which confirms that
bridged midblocks contribute more to the tensile properties than do entangled midblocks. The second observation worth mentioning is that, as $\psi$ increases, $G_0f$ decreases almost linearly, verifying that the population of bridged midblocks decreases as SEPS copolymers are replaced with SEP copolymers. In the case of the TPEG series with $\phi = 10$ wt%, the STN model fails to yield realistic values for the model parameters, most likely due to the extreme softness of the material. According to Fig. 3.3a, adding diblock copolymer to the TPEG does not significantly affect the mechanical response. Since these formulations contain, at most, 10 wt% SEPS copolymer (at $\psi = 0$ wt%), the population of bridged midblocks in these TPEGs is expected to be much lower than that encountered in systems with $\phi = 30$ wt%. Thus, addition of SEP to the TPEGs with $\phi = 10$ wt% has little effect on the fraction of bridged midblocks and produces no discernible differences.

Since these TPEGs are under consideration as DEs for EAP applications, their cyclic strain hysteresis must be evaluated, as DEs can be subjected to millions of actuation cycles during their active lifetime. Following the approach reported by Shankar et al., we have repeatedly strained samples to 400% for 100 cycles at a fixed rate of 127 mm/min. In Fig. 3.5, data corresponding to the 1$^{st}$, 2$^{nd}$ and 100$^{th}$ strain cycles of TPEGs with $\phi = 30$ wt% are presented for two extreme values of $\psi$ (0 and 50 wt% in Figs. 3.5a, and 3.5b, respectively). Cyclic stress-stretch behavior assessed at intermediate compositions lies between the two limits shown. As the number of cycles is increased, the loading-unloading cycles shift slightly to lower stresses, although we point out that there is not much difference in the areas of each loading-unloading cycle, which provides an indication of dissipative loss. The
unrecoverable strain after the 100th cycle of the TPEG with $\psi = 0$ wt% is ~7%, whereas that for the TPEG with $\psi = 50$ is ~20%. A diblock-induced increase in cyclic hysteresis can be explained in terms of the dangling EP midblocks of SEP in the swollen rubbery matrix. During large extensions, dangling midblock tails disentangle and adopt new conformations in an effort to relax. As the population of EP blocks deposited from the SEP diblock copolymer increases with increasing $\psi$, this effect becomes increasingly more pronounced, leading to a progressive increase in cyclic losses. The TPEGs with $\phi = 10$ wt% (data not shown) show evidence of negligible unrecoverable strain and a nearly elastic response.

When TPEGs, as well as conventional chemically cross-linked elastomers, are employed as DEs, a biaxial mechanical prestrain is routinely applied to reduce the film thickness and the electric potential required for actuation by increasing the magnitude of the electric field. Recent efforts have established that TPEGs derived from acrylic thermoplastic elastomers do not require mechanical prestrain to achieve actuation strains beyond 100%.11 In most reported cases, styrenic TPEGs are subjected to an equibiaxial prestrain of 300% prior to actuation.10, 18 For consistency with previous efforts, we apply the same level of mechanical prestrain to the TPEGs under investigation here. It is important to realize at this juncture that, due to diblock-induced changes in network connectivity, the prestrained materials prepared for actuation tests will undoubtedly possess different (electro)mechanical properties. Softened materials with a high diblock concentration, for example, are expected to yield higher actuation strains for a given electric field and also require a lower electric field for a given actuation strain. The electrical actuation response of TPEGs with 10 and 30 wt% copolymer is displayed in Figs. 3.6a and 3.6b, respectively. In Fig. 3.6a, addition of diblock
copolymers to the TPEG is responsible for promoting a marginal increase in the maximum actuation strain, but pronounced reductions in the electric field required to induce actuation and cause failure (at the dielectric breakdown field). Similar, and more systematic, reductions are evident in Fig. 3.6b. While the actuation strains are also dependent on the concentration of added diblock copolymer, the maximum actuation strain does not vary methodically with $\psi$. We hasten to point out that the maximum actuation strains reported here for the TPEG formulations with no diblock copolymer are lower than what has been previously reported$^{11}$ due to a difference in film thickness. Initial film thickness independent of mechanical prestrain has recently been found to have a profound effect on electrical actuation behavior.$^{19}$

In Fig. 3.7, actuation strains measured from TPEGs with 10 and 30 wt% copolymer at comparable fixed electric fields are presented as a function of diblock concentration. The effect of material softening as $\psi$ is increased is clearly visible for the TPEG with $\phi = 30$ wt%. A similar trend with composition is not apparent for the softer TPEG with $\phi = 10$ wt%, which agrees with our earlier observations regarding tensile deformation behavior. Nonetheless, the observations reported here indicate that the proposed strategy of blending a matched diblock copolymer with a network-forming triblock copolymer to design new TPEGs for use as DEs is viable and can be used to obtain materials with targeted stress-strain behavior for optimum actuator performance.
Figure 3.1 Schematic showing the networks formed by (a) SEPS copolymers and (b) blend of SEP and SEPS copolymers. Blue and green contours represent swollen EP blocks of SEPS and SEP respectively. In (b), 4 SEPS chains in (a) are replaced by 8 matched SEP chains. Red spheres represent S block micelles.
Figure 3.2 Moduli as a function of $\phi$ and $\psi$. 
Figure 3.3 Representative stress-stretch curves different $\varphi$s (labeled). The concentrations of diblock are labeled. In (a) lines are guide for eyes, while in (b) lines are STN fits.
Figure 3.4 STN parameter for $\phi = 30$ wt%. For $\phi = 30$ wt% the model did not give good fits.
Figure 3.5 The hysteresis behavior of blends with $\phi = 30$ wt% for the lowest and highest $\psi$ used (labeled). When $\phi = 10$ wt%, no difference was seen with $\psi$ and also within the cycles.
(the data is not shown). Colors represent different cycle numbers: green (cycle 1), blue (cycle 2) and pink (cycle 100).

Figure 3.6 Actuation as a function of electric field (E) for 10 (a) wt% and $\phi_s = 30$ (b). The lines are guide for eyes.
Figure 3.7 Actuation at a fixed electric fields (E) (labeled) shown for both $\varphi = 30$ and 10 wt% (labeled).
References


4 Prestrain-free Dielectric Elastomers based on Acrylic Thermoplastic Elastomer Gels: A Morphological and (Electro)Mechanical Property Study

Recent efforts have established that thermoplastic elastomer gels (TPEGs) composed of styrenic triblock copolymers swollen with a midblock-selective solvent exhibit remarkable electromechanical properties as high-performance dielectric elastomers. This class of electro-active polymers typically requires high electric fields for actuation, and a shortcoming that continues to thwart the widespread commercialization of such materials in general is the need to apply mechanical prestrain prior to electroactuation to decrease film thickness and, thus, the electric potential required to promote actuation. To alleviate this requirement, we investigate TPEGs consisting of acrylic triblock copolymers differing in molecular weight and composition, and swollen with a high dielectric, midblock-selective solvent. Synchrotron small-angle x-ray scattering is used to probe the nanoscale morphologies of the resultant materials, and analysis of quasi-static and cyclic tensile properties provides additional insight into both blend morphologies and electroactuation efficacy. Actuation strains measured in the absence of mechanical prestrain exceed 100% on an area basis, and electric fields capable of inducing actuation are as low as ~20 kV/mm. Failure occurs by either electromechanical instability or dielectric breakdown, depending on the copolymer and TPEG composition employed. The electromechanical properties of these acrylic-based TPEGs match or exceed those of skeletal muscle, in which case they constitute an attractive and unexplored alternative to existing dielectric elastomers.
4.1 Introduction

Triblock copolymers composed of glassy A endblocks and a rubbery B midblock are commonly classified as thermoplastic elastomers\(^{[1]}\) (TPEs) and can be swollen with a low-volatility B-selective solvent to yield thermoplastic elastomer gels\(^{[2-4]}\) (TPEGs), which continue to garner considerable scientific and technological interest as broadly functional materials. At copolymer concentrations below the critical micelle concentration (cmc), copolymer molecules remain in solution as unimers. As the copolymer concentration is increased above the cmc, however, micelles develop as the solvent-incompatible endblocks aggregate to form a glassy core within a solvated shell of the solvent-compatible midblock.\(^{[5]}\)

Between the cmc and the critical gel concentration (cgc), so-called "flowered" micelles are sufficiently distant that the B midblocks form loops, wherein both ends of a copolymer molecule reside in the same micelle, or, to a lesser extent, thermodynamically unfavorable dangling ends, in which one endblock is located within a micelle and the other remains in the incompatible solvent matrix. At the cgc, the micelles are sufficiently close to permit the midblocks to connect (i.e., bridge) adjacent micelles and thus form a network physically stabilized by glassy cross-link sites.\(^{[2,6]}\) The morphological features and mechanical properties of such gels depend sensitively on several material factors including copolymer composition, molecular weight and concentration, as well as solvent quality and free volume.\(^{[7,8]}\) Most of the TPEGs studied thus far are based on styrenic copolymers, that is, copolymers with polystyrene endblocks and polydiene or polyolefin midblocks. Such TPEGs have gained tremendous attention as vibration dampeners,\(^{[9]}\) pressure-sensitive adhesives,\(^{[10]}\) microfluidic substrates,\(^{[11]}\) and, most recently, dielectric elastomers.\(^{[12]}\)
Another family of emerging TPEs relies on acrylic, rather than styrenic, endblocks to improve properties such as UV resistance and thermal stability over a broadened temperature range (due to a higher upper glass transition temperature, $T_g$).\textsuperscript{[13]} The endblocks of such TPEs are frequently atactic poly(methyl methacrylate) (PMMA) with a $T_g$ in excess of 120°C, and the midblock is typically a low-$T_g$ acrylate rubber such as poly($n$-butyl acrylate) (PnBA), which possesses a $T_g$ of about -50°C at infinite molecular weight. Addition of a midblock-selective solvent to an acrylic TPE yields acrylic gels (ATPEGs) that are relatively new and unexplored. Shull and co-workers\textsuperscript{[14,15]} have pioneered this field by investigating the morphological characteristics and mechanical properties of such materials intended for use as adhesives. In their studies, they have employed high-vapor-pressure alcohols as the midblock-selective solvents, and the copolymer concentrations examined span the dilute to semi-dilute regimes. In this work, ATPEGs composed of two different PMMA-\textit{b}-PnBA-\textit{b}-PMMA (MBM) triblock copolymers differing in molecular weight and composition are examined in the presence of dioctyl phthalate (DOP), a midblock-selective solvent with a high normal boiling point (384°C). Since most prior efforts have analyzed ATPEGs stabilized by spherical micelles, the present study is restricted to the concentrated copolymer regime so that structure-property relationships of ATPEGs possessing non-spherical morphologies can be elucidated. Moreover, these materials exhibit electroactuation properties that make them uniquely attractive as dielectric elastomers (DEs).

Electroactive polymers are macromolecules that are generally capable of changing their size and shape in response to the application of an external electric potential. As a growing class of electroactive polymers that shows tremendous promise for use in diverse
technologies ranging from micro air vehicles and mini/microrobotics to flat panel speakers and responsive prosthetics, DEs, or electroelastomers, operate on the principle of electrostatic actuation in the presence of an applied electric field.\textsuperscript{[16-20]} Actuation in this case results from the development of a compressive Maxwell stress, as described in more detail in the following section. Unlike their inorganic counterparts (\textit{e.g.}, shape-memory alloys,\textsuperscript{[21]} carbon nanotubes\textsuperscript{[22]} and piezoelectric ceramics\textsuperscript{[23]}), DEs are relatively inexpensive, lightweight, mechanically robust, and scalable. They can afford exceptionally large actuation strains (~300\%), high energy densities (>8 MJ/m\textsuperscript{3}), high electromechanical coupling efficiencies (>90\%), and low cycling hysteresis.\textsuperscript{[4]} Our previous studies of DEs derived from styrenic copolymers selectively swollen with a largely aliphatic mineral oil have repeatedly demonstrated that TPEGs are ideally suited for this nontraditional application and, unlike conventional DEs produced from chemically cross-linked elastomers,\textsuperscript{[24]} provide unprecedented versatility with regard to property design. Two drawbacks, however, continue to plague the commercialization of DEs: \textit{(i)} a high electric field (typically ranging from \textit{ca.} 20 to over 200 kV/mm) is required to induce electrical actuation, and \textit{(ii)} mechanical prestrain is commonly needed to reduce specimen thickness and therefore lower the voltage required for actuation. The latter, in particular, necessitates a rigid support frame that is accompanied by added weight and space, and raises mechanical property concerns regarding long-time stress relaxation of the DE and premature failure of the DE upon cycling due to stress concentration along the frame. In the present study, we demonstrate that ATPEGs employed as nanostructured DEs can overcome both of the inherent shortcomings of contemporary DEs.
4.2 Electroactuation background

The mechanism by which DEs undergo electrical actuation derives from the electrostatic force of attraction between two oppositely charged compliant electrodes on opposing sides of a DE film. As portrayed in Fig. 4.1, this force induces a Maxwell stress ($\sigma_M$), the magnitude of which for an ideal DE is given by:\[16\]

$$\sigma_M = \varepsilon_0\varepsilon E^2$$  \hspace{1cm} (1)

where $\varepsilon_0$ and $\varepsilon$ denote the permittivity of free space and the dielectric constant of the DE, respectively, and $E$ represents the electric field arising from the voltage applied across the film thickness. The resulting actuation causes the film thickness to decrease while the active area corresponding to the compliant electrode expands in an isochoric process. The actuation strain (reported here on an area basis) is determined from the change in active area relative to the initial active area in the circular test configuration conventionally used to analyze the electroactuation of DEs. Alternatively, the transverse strain in the film thickness direction can be computed or measured directly.$^{[19]}$ Other important performance measures include the electromechanical coupling efficiency ($K^2$), which provides a measure of the conversion of electrical energy to mechanical work, and the energy density ($F$), which corresponds to the amount of electrical energy that is converted to mechanical work per volume of material per cycle.$^{[16]}$ In a recent study,$^{[25]}$ of DEs composed of styrenic TPEGs, the ultimate electromechanical properties achieved during actuation — namely, the maximum actuation strain and the dielectric breakdown strength (i.e., the electric field at which failure occurs) — have been shown to depend on both the level of mechanical prestrain and the initial specimen thickness. If the copolymer used to prepare the TPEG is of sufficiently low molecular weight,
maximum actuation strains of up to 20% and $K^2$ values of up to 30% can be realized\textsuperscript{[26]} without mechanical prestrain prior to electroactuation. This response, although promising and superior to that of VHB (the benchmark DE composed of an acrylic elastomer and available as adhesive tape from 3M Co.), is insufficient for applications that, for example, emulate mammalian muscle, which exhibits higher performance metrics (\textit{cf.} Table 1).\textsuperscript{[4,17,26]} As anticipated, the electric fields and, hence, voltages needed to induce actuation in these tests are disappointingly higher than those required after mechanical prestrain.

4.3 Experimental

4.3.1 Materials

Two commercial MBM triblock copolymers were used in this study, and their designations, molecular characteristics and manufacturers are listed in Table 2. Reagent-grade DOP (98% purity) and toluene were purchased from Fisher Scientific and silver grease (\textit{i.e.}, silver particles suspended in a silicone matrix) was obtained from Chemtronics Circuit Works (Kennesaw, GA).

4.3.2 Methods

\textit{Sample Preparation.} Each sample was prepared by dissolving predetermined quantities of copolymer and DOP, along with 1 wt\% Irganox 1010 (as an antioxidant) relative to the copolymer concentration, in toluene and then casting the resultant solution in a Teflon tray
and permitting the toluene to evaporate over 2 days. The ensuing film was annealed at 135°C for 12 h under vacuum to remove residual toluene and subsequently melt-pressed at 135°C to a uniform specimen thickness of 0.1-0.2 mm. The copolymer concentration in each ATPEG series ranged between 45 and 65 wt% in 5 wt% increments (this range corresponds to 20-30 vol% in the MBM104 series and 12-18 vol% in the MBM146 series). The ATPEGs produced in this fashion were designated as MBMm-c, where m denotes the number-average molecular weight of the copolymer (in kDa) and c indicates the copolymer concentration (in wt%). Comparisons made with other block copolymer systems follow the same naming convention. For example, SEBS75-45 identifies a TPEG composed of a poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) triblock copolymer with a molecular weight of 75 kDa at a concentration of 45 wt% copolymer.

Morphological characteristics. Morphological features of ATPEGs from both copolymer series were deduced by small-angle X-ray scattering (SAXS) performed at 10 kV on beamline 7.3.3 of the Advanced Light Source at the Lawrence Berkeley National Laboratory. The beam size was 0.1 mm x 0.1 mm, and the sample-to-detector distance was held constant at 2.3 m. Two-dimensional scattering patterns were collected on a Pilatus 1M detector after an exposure time of 20 s and then azimuthally integrated and radially averaged to yield 1D profiles. In these profiles, scattered intensity was determined as a function of wave vector (q) given by \((4\pi/\lambda)\sin(\theta/2)\), where \(\lambda\) is the wavelength of the X-ray beam (0.1240 nm at 10 kV) and \(\theta\) is the scattering angle, after correcting for dark background, specimen transmittance, pixel efficiency, and spatial heterogeneities in the beam. Specimens were heated to a target
temperature at a rate of 10°C/min and held at that temperature for 10 min to achieve thermal equilibration prior to data acquisition.

*Mechanical and thermal properties.* Each ATPEG examined here was subjected to uniaxial tensile testing on a computer-controlled MTS-30G load frame, and tests were performed to failure at a constant crosshead speed of 127 mm/min at ambient temperature. Properties such as the tensile modulus, strength at break and elongation at break were measured from the resulting nominal stress-strain plots. To discern the extent to which these ATPEGs exhibit hysteresis upon cyclic deformation, two types of strain cycling tests were conducted. In the first, each ATPEG was cycled (loading-unloading) 30x up to 100% strain. After 30 cycles, the non-recoverable strain (set) was evaluated. The peak stress corresponding to 100% strain in each cycle was recorded to ascertain the extent of stress relaxation. In the second type of test, a specimen was strained to a selected stress value ($\sigma_{\text{max}}$) and released to a lower stress value ($\sigma_{\text{min}}$) chosen so that specimen slack was avoided. After completion of a cycle, $\sigma_{\text{max}}$ was increased incrementally and the loading-unloading cycle was repeated with $\sigma_{\text{min}}$ unchanged. This process was continued until $\sigma_{\text{max}}$ approached the stress determined from the quasi-static uniaxial tensile tests performed to failure. To discern the effect of DOP on the thermal characteristics of the ATPEGs, differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 instrument operated from -125 to 170°C at a constant heating/cooling rate of 10°C/min under nitrogen. Glass transition temperatures were identified as points of inflection from second-heat thermograms.
**Electromechanical properties.** The electroactuation behavior of each ATPEG was assessed at 0% mechanical prestrain unless otherwise noted. For this purpose, a circular active area was created on each test specimen by applying compliant electrodes (silver grease) on both sides of the specimen while the specimen was held in a circular, rigid test frame. Edge effects were precluded by ensuring that the active electrode area was small relative to the film area. The electrodes were connected to a Bertan 225-30R high-voltage power supply (Spellman High Voltage Electronics Corp., Hauppauge, NY), and actuation was induced by an automated voltage trigger. The voltage was ramped at 250 V/s until the specimen being tested underwent breakdown. As the voltage was ramped, in-plane expansion of the active area was digitally recorded, and the resulting footage was analyzed frame-by-frame with the MATROX® Inspector 4.0 software package to determine the corresponding actuation strain. Dielectric constants of all the ATPEGs were measured in film form with a dielectric test fixture (Agilent 16451B) connected to an LCR meter (HP4284A) operated at 25°C from 20 to 10^6 Hz.

4.4 Results and Discussion

4.4.1 Morphological characteristics

As shown in Fig. 4.2, SAXS profiles acquired above the T_g of the M endblocks (106°C in MBM104 and 121°C in MBM146, according to the DSC results listed in Table 3) at 135°C (except for MBM104-45) provide insight into the melt morphologies of the ATPEGs examined here, since they are processed at that temperature (see the Experimental section).
Here, only select scans relevant to the present work are shown, and a detailed account of additional results will be forthcoming. Peak ratios relative to the principal peak in the structure factor reveal the symmetry of the existing morphology. Peak ratios of $1:2:3:4$, $1:3:2:4$, and $1:2:3:4$ correspond to the classical morphologies: spheres on a body-centered cubic (bcc) lattice, cylinders on a hexagonal lattice and alternating lamellae, respectively. When the volume fractions of the endblocks are considered (20-30 vol% for MBM104 and 12-18 vol% M for MBM146), the morphologies that could be unambiguously assigned on the basis of peak ratios match well with the morphologies observed in styrenic TPEGs. Since the MBM104 molecules are shorter than the MBM146 chains and are therefore able to self-organize more readily, long-range order is expected to be more fully developed in the ATPEGs generated from the MBM104 copolymer. On the basis of the peak ratios in the SAXS patterns displayed in Figs. 4.2a and 4.3a, the morphologies of the ATPEGs ranging in copolymer concentration from 50 to 65 wt% can be described as hexagonally-packed cylinders. Since higher-order peaks are not evident in the MBM104-45 system, the corresponding morphology could not be assigned with confidence. At the opposite extreme, the neat (i.e., non-solvated) copolymer is found to possess the lamellar morphology, which is consistent with the composition of the copolymer (~48 vol% M).

In the case of the ATPEGs produced from the MBM146 copolymer (cf. Fig. 4.2b), only the morphology of the MBM146-45 formulation is clearly classified (as bcc spheres) from SAXS. At concentrations ranging from 50 to 65 wt% copolymer, the SAXS patterns appear similar, in which case these ATPEGs most likely possess identical morphologies. Regrettably, the lack of peaks in these patterns do not permit unambiguous discrimination.
between bcc spheres and hexagonally-packed cylinders (see Table 4). Elucidating these morphologies by electron microscopy, as well as the existence of order-(dis)order transitions by rheology and SAXS, is the focus of ongoing research and will be reported in a future publication. The neat MBM146 copolymer possesses a cylindrical morphology, which is consistent with the copolymer composition (~29 vol% M). This assignment further indicates that the unclassified morphologies exist between bcc spheres and hexagonally-packed cylinders and may represent a coexisting, frustrated mixture of the two or a nonequilibrated intermediate morphology (e.g., undulating cylinders), especially since the peak in the vicinity of 0.45 nm\(^{-1}\) is clearly present in each of the patterns. These morphological differences within and between the two ATPEG series can be reasonably expected to affect the corresponding (electro)mechanical properties, as interrogated in the following sections. Since all of the (electro)mechanical tests are conducted at ambient temperature, it is important to note that the morphologies identified in Fig. 4.2 persist as the pure copolymers and their respective ATPEGs are cooled to ambient temperature, as evidenced by the SAXS patterns collected closer to ambient temperature (at 35°C) and displayed in Fig. 4.3. In this case, the endblocks are glassy, and shifts in the principal peak reflect dimensional changes that are introduced during vitrification. Comparison of the patterns in Figs. 4.2 and 4.3 indicate that the morphologies classified at 135°C are most likely retained upon vitrification of the M endblocks.
4.4.2 Mechanical properties

Representative nominal stress-strain curves are shown in Fig. 4.4 for ATPEGs in both copolymer series: (a) MBM146 and (b) MBM104. Several important features are evident in this figure. The first is that an increase in copolymer concentration is accompanied by increases in both the tensile modulus and the strength at failure in both series. These relationships are explicitly provided in Figs. 4.5a and 4.5b, respectively, and demonstrate that, in both cases, the mechanical properties of the ATPEGs derived from the MBM104 copolymer are more sensitive to copolymer concentration (due presumably to its higher M content) than are those containing the MBM146 copolymer. These property changes constitute a general consequence of increasing the concentration of the glassy M endblocks and are comparable to reports of styrenic copolymers in which the styrene content dominates the mechanical behavior.\[27] The increase in modulus can be attributed to the effect of a reinforcing filler, \textit{viz.}, the M microdomains, whose population and size increase with increasing copolymer concentration. This explanation agrees favorably with the results of Seitz et al.,\[28] who reported that the glassy domains in MBM-based ATPEGs influence the mechanical properties more than the network formed by bridged B midblocks. In general, the elongation at break likewise decreases (by comparable extents in both series) with decreasing copolymer concentration and can most likely be attributed to enhanced plasticization of the glassy M domains with DOP, as evidenced by lower glass transition temperatures at elevated DOP concentrations (from thermal calorimetry, data not shown).

Comparison of the two copolymer series in Fig. 4.4 also reveals a profound difference in stress evolution with strain. As above, the apparent stress-strain behavior can be interpreted
in terms of the higher glassy content in ATPEGs consisting of the MBM104 copolymer. The steep rise in stress at low strain levels, the higher moduli and consequently higher stress values at break in the MBM104 series are due to the higher glassy content relative to the MBM146 series. Strain softening at intermediate strain levels (~200%) is a common characteristic of TPEGs, but is not observed in most of the MBM104 series in Fig. 4.4b. One plausible explanation for this observation, as well as the higher moduli, is that cylinders, not spheres, exist in formulations with 50–65 wt% copolymer in the MBM104 series and offer greater resistance to deformation at low strains than do spheres. Laurer et al.\cite{27} and Seitz et al.\cite{28} independently report that cylindrical morphologies possess higher moduli than spherical ones in TPEGs and ATPEGs, respectively. At higher strains near failure, formulations in the MBM146 series in Fig. 4.4a exhibit significant strain hardening as the midblocks approach full extension. In sharp contrast, ATPEGs derived from the MBM104 copolymer display evidence of strain softening at this limit in Fig. 4.4b due to irreversible deformation and damage to the glassy M microdomains. Thus, the results presented in Figs. 4.4 and 4.5 establish that the two ATPEG series considered in this study possess markedly different mechanical properties that relate to copolymer composition and morphology.

As DEs, these ATPEGs are required to withstand cyclic deformation. To determine their ability to do so, we have subjected them to multicycle uniaxial tensile deformation in two types of strain-cycling tests. In the first, specimens are cycled 30x between 0 and 100% strain, and the results are shown in Fig. 4.6 for two formulations (45 and 60 wt% copolymer) in the MBM104 and MBM146 series. In all cases examined, the nominal stress-strain response becomes independent of cycle number after about 25 cycles, which indicates that
our choice of 30 cycles is sufficient to ascertain the cyclic deformation behavior of the present materials. To facilitate scrutinization of the data in Fig. 4.6, only the 1st, 2nd and 30th loading-unloading loops are shown. In Fig. 4.6a, the MBM146-45 formulation exhibits virtually indistinguishable loading-unloading loops with complete elastic recovery and nearly no hysteresis (the level of unrecoverable strain is <5%) upon repeated tensile deformation, which is strikingly reminiscent of styrenic TPEGs discussed elsewhere.\cite{29} Minimal stress softening is also apparent in multiple loading and unloading cycles over the strain range examined. Figure 4.6b shows, however, that the MBM146-60 formulation is more sensitive to cyclic loading and undergoes limited hysteresis, as evidenced by a small shift in the data at zero load to a higher unrecoverable strain (set) after just one cycle. After 30 cycles, however, the set remains at less than 10% strain. This specimen also undergoes stress softening that becomes detectable after the second cycle and that increases slightly with copolymer concentration. According to the results provided in Fig. 4.7, the degree of stress softening, as determined from a reduction in the ratio of the peak stress measured at 100% strain ($\sigma_n$) during each cycle (n) to that measured after the first cycle ($\sigma_1$), remains negligibly small for all the ATPEGs produced from the MBM146 copolymer.

On the basis of their minimal hysteresis, set and stress softening due to cyclic deformation, it immediately follows that the MBM146-based ATPEGs appear suitable for use in continuous electroactuation applications. This is not the case, however, for formulations derived from the MBM104 copolymer. In Figs. 4.6c and 4.6d, corresponding to the MBM104-45 and MBM104-60 systems, hysteretic losses due to cycling are pronounced and become progressively worse as the copolymer concentration is increased. Stress
softening is clearly discernible in all these ATPEGs and increases with increasing copolymer concentration (cf. Fig. 4.7). For comparative purposes, the value of $\sigma_{30}/\sigma_1$ for the MBM104-65 formulation is 50%, in marked contrast to 96% for the MBM146-65 formulation under identical test conditions. Similarly, values of the set measured for both ATPEG series and included in Fig. 4.8 confirm that those generated from the MBM104 copolymer are considerably more sensitive to cycling than those derived from the MBM146 copolymer. In fact, set values determined for formulations with the MBM146 copolymer are typically less than or equal to 5%, whereas those for materials incorporating the MBM104 copolymer can exceed 35% after 30 cycles, suggesting that these systems may not be suited for use as actuators that could require millions of strain cycles during their active lifetime.

The mechanical properties of the ATPEGs under investigation here can be explained in light of their nanoscale morphologies. The prominent hysteresis loops, set and stress softening displayed by the MBM104-based ATPEGs upon cycling are largely attributed to the permanent deformation of glassy M microdomains that, as cylinders, are discrete but potentially long and intertwined. In this case, the cyclic mechanical properties of network materials possessing anisotropic glassy microdomains are expected to display evidence of viscoelasticity, unlike analogous systems containing uniformly-dispersed, spherical M microdomains. Recall, for instance, that the MBM146-45 formulation possesses a spherical morphology according to SAXS (cf. Figs. 4.2 and 4.3) and exhibits a nearly elastic response to cyclic deformation in Fig. 4.6a. Comparable behavior is retained when the strain is doubled to 200%. These observations support the findings of Seitz et al. and Mamodia, who report that discretely distributed spheres suffer negligible deformation under uniaxial
tension. Even under biaxial tension, the deformation of glassy spheres in a TPEG is minimal. Another consideration here is the fraction of bridged midblocks, which dictates the connectivity of the network responsible for the mechanical integrity, as well as the recoverability, of a swollen triblock copolymer subjected to deformation. Matsen and Thompson predict, on the basis of self-consistent field theory, that the fraction of bridged midblocks is the largest for the spherical morphology, in which case it immediately follows that the restorative capability of the midblock network decreases upon changing from a spherical to a cylindrical morphology.

Although the bridging fraction may differ considerably between spherical and cylindrical block copolymer morphologies, we do not believe that the bridge fraction changes appreciably during cyclic loading. The ATPEG series derived from the MBM104 copolymer, for instance, exhibits permanent deformation in all the formulations examined here. Except for MBM104-45 (whose morphology cannot be classified from SAXS), all other formulations possess hexagonally-packed cylinders, according to the SAXS patterns provided in Figs. 4.2 and 4.3. In cyclic loading tests, the maximum damage to the material occurs during the first loading cycle, after which subsequent damage continues incrementally in subsequent cycles. Recovery achieved during the unloading cycles is due almost exclusively to the bridged midblocks. If M endblocks were to pull out from glassy micelles during deformation, the population of bridged midblocks would decrease and the unloading behavior, in turn, would most likely continue to evolve as the number of cycles increased.

According to the data presented in Figs. 4.6c and 4.6d (as well as additional data not shown for other formulations), the unloading curves appear similar in each cycle, strongly
suggesting that the bridging fraction remains unchanged during tensile deformation under the test conditions employed here. Since the tests have been performed at ambient temperature (below $T_g$ of the M blocks), we instead suspect that fracture or otherwise permanent deformation of the glassy cylindrical microdomains under loads exceeding their elastic limit is responsible for the results displayed in Figs. 4.6-4.8. Results from the second cycling test (described in detail below) are consistent with this conclusion. In these tests, samples subjected to increasing stress after a single cycle to a predetermined stress show evidence of additional energy dissipation, softening and set consistent with increased deformation and/or fracture of the M cylinders. Similar behavior independently reported for ATPEGs on the basis of compression testing$^{[15]}$ and indentation techniques$^{[28]}$ has been ascribed to morphological differences deduced solely on the basis of composition.

Stress softening (cf. Fig. 4.7) is a frequently encountered phenomenon widely referred to as the Mullins effect in filled rubbers$^{[33]}$ and crystallizing gums.$^{[34]}$ It has been interpreted$^{[35]}$ in terms of molecular-level processes such as molecular slippage, chain breakage and chain disentanglement and is manifested as a significant reduction in stress. Recently, this effect has been reported to occur in styrenic TPEs due to either strain-induced crystallization of the polyolefin midblocks (which depends on midblock composition and chain length) or microbuckling of glassy cylindrical or lamellar microdomains.$^{[30,36]}$ In the present study, midblock crystallization in the presence of DOP can be immediately ruled out, and so we only consider further the second possibility. To determine if the present ATPEGs display evidence of the Mullins effect, cyclic tensile tests have been performed between two stresses — a maximum ($\sigma_{\text{max}}$) and a minimum ($\sigma_{\text{min}}$) — with $\sigma_{\text{max}}$ increased stepwise after
completion of each cycle. Representative test results are provided in Fig. 4.9 for formulations containing 60 wt% copolymer in both series. Several features in this figure warrant discussion. The nominal stress-strain curves corresponding to loading and unloading in Figs. 4.9a and 4.9b are strongly nonlinear and reminiscent of the data shown earlier in Figs. 4.6b and 4.6d, respectively. The hysteresis energy, as determined from the area between the loading and unloading curves in each cycle, increases noticeably as $\sigma_{\text{max}}$ is increased in both systems and is attributed to an increase in the strain-induced damage to the glassy microdomains. When $\sigma_{\text{max}}$ is subsequently increased after completing a loading–unloading cycle at a given stress, the stress–strain curve rapidly reaches the quasi-static tensile curve (cf. Fig. 4.4) measured at the same composition (identified by open circles in Fig. 4.9). According to Roos and Creton\textsuperscript{[9]} and Drozdov,\textsuperscript{[37]} this characteristic is a signature feature of the Mullins effect, thereby confirming our earlier conclusion.

On one hand, the Mullins effect is apparent at all compositions in the MBM104-based ATPEG series (data not shown), and it becomes more pronounced as the copolymer concentration is increased from 45 to 65 wt%. In the MBM146-45 formulation, on the other hand, evidence of the Mullins effect is completely absent, but becomes increasingly discernible with increasing polymer concentration. These observations are likewise consistent with the ATPEG morphologies assigned from SAXS, as well as the observations reported by Mamodia\textsuperscript{[30]} for neat styrenic triblock copolymers. Glassy cylinders (in the MBM104 series) can undergo microbuckling and form a chevron-type pattern, which results in the Mullins effect. The increase in this effect with increasing copolymer concentration may reflect corresponding changes in the dimensions of the glassy cylinders, since resistance
to fracture or permanent deformation depends on both cylinder size and modulus.\textsuperscript{[36]}

Although an experimentally corroborated correlation is not yet established between microdomain stiffness and the Mullins effect, variation in microdomain size with copolymer concentration could help to explain the property trends ascertained in the MBM104-based ATPEG series. In Figs. 4.2a and 4.3a, for instance, the principal peak systematically broadens (which means that the cylindrical diameter correspondingly decreases) as the copolymer concentration is increased. This variation suggests that the Mullins effect, under comparable load cycling, becomes increasingly pronounced as the glassy cylinders become thinner. This observation is certainly amenable to further experimental verification and computer simulation. In the one formulation possessing an unequivocal spherical morphology (MBM146-45), no microbuckling of the glassy microdomains can occur and, hence, no Mullins effect is observed.

In the discussion above, we demonstrate that the Mullins effect is a consequence of the cylindrical microdomains in the ATPEGs produced from the MBM104 copolymer. Can this relationship help to identify the unclassified morphologies in the MBM104 and MBM146 series? Although electron microscopy, coupled with electron tomography\textsuperscript{[38]} when necessary, is conventionally used to identify the morphology of microphase-separated block copolymer systems, the M and B blocks of the parent MBM copolymers are chemically similar and, as acrylics, are inherently resistant to most heavy-metal stains, thereby making selective staining to enhance phase contrast difficult, if at all possible. While such efforts remain underway, we turn our attention to an alternative and somewhat unconventional approach to morphological determination. If the SAXS patterns displayed in Figs. 4.2 and 4.3 are
considered in light of the mechanical property results provided in Figs. 4.6-4.9, then additional insight into the morphologies of the unclassified formulations can be gleaned. First, recall that the undetermined MBM146 morphologies possess similar scattering patterns and are therefore considered to be the same. Second, these morphologies are likely to be dispersed since they reside between hexagonally-packed cylinders (MBM146-100) and bcc spheres (MBM146-45). Since spherical morphologies do not show evidence of the Mullins effect, the unclassified morphologies in the MBM146 series are most likely not spherical in nature. As they exhibit the Mullins effect to a relatively small degree, however, we suspect that the morphology is slightly anisotropic (to permit detectable strain-induced microdomain fracture or permanent deformation). Morphologies consistent with these requirements include short, stubby cylinders or, alternatively, ellipsoids that, because of their slight anisotropy, do not readily arrange on a lattice. Another possibility is a mixed morphology composed of spheres with a small fraction of cylinders that frustrate lattice packing and undergo strain-induced damage upon cycling. In the case of the undetermined MBM104-45 formulation, the Mullins effect is also clearly encountered. This feature, combined with the composition of this material (24 vol% M), strongly suggests that the morphology in this ATPEG is either cylindrical or a mixture of cylinders and spheres.

4.4.3 Electromechanical properties

Interest in selectively swollen triblock copolymer systems as DEs capable of being finely tuned in the manner by which they respond to an applied electric fields continues to grow, and this study represents the first attempt to employ ATPEGs for the purpose of being used
as electromechanical actuators. While previous investigations of ATPEGs have utilized midblock-selective solvents with relatively high vapor pressures suitable for materials processing, use of high-boiling DOP as the midblock extender in the present study permits extended stabilization of the resulting materials for application purposes. Preferential compatibility between the copolymer midblock and DOP can be explained in terms of their solubility parameters (\(\delta\)). The value of \(\delta\) for the B midblock \([9.1 \text{ (cal/cm}^3\text{)}^{1/2}]^{[39]}\) is marginally closer to that of DOP \([7.9 \text{ (cal/cm}^3\text{)}^{1/2}]^{[40]}\) than is \(\delta\) of the M endblock \([9.3 \text{ (cal/cm}^3\text{)}^{1/2}]^{[39]}\).

The difference in solvent quality relative to the copolymer blocks, coupled with the compositions and molecular weights of the two copolymers and the solvent concentrations examined, promotes micellization (spherical, cylindrical or an intermediate/mixture thereof) of M blocks embedded in a matrix of B blocks swollen with DOP. Due to the similarity in the chemical nature (and solubility parameters) of the blocks comprising the copolymers, however, the solubility of DOP in M cannot be ignored, in which case it is reasonable to expect that the micelles containing M cores are somewhat swollen by DOP. An undesirable ramification of DOP in the micellar cores is a reduction in the upper \(T_g\) due to plasticization of the endblocks, which serve as the physical cross-links responsible for network stabilization. Analysis of these depressed \(T_g\) values (listed in Table 3) by the Fox-Flory equation indicates that the DOP concentration within the micellar cores ranges from 3 to 17 wt%.

The mechanical properties reflecting the presence of a supramolecular micellar network and interrogated in the previous section confirm that at least some of the present ATPEGs are suitable candidates as DEs on the basis of their response to strain cycling. In this section, the
dependence of electrical actuation without mechanical prestrain on copolymer concentration is ascertained for both series of ATPEGs and quantitatively compared with two other DEs previously measured under comparable test conditions.\cite{26} (i) a SEBS75-45 TPEG composed of a styrenic triblock copolymer and reported to attain a maximum actuation strain of 7% with no mechanical prestrain, and (ii) the benchmark acrylic elastomer VHB4910, where the last 2 digits identify film thickness (in tenths of a millimeter). Recall that electroactuation depends on the development of a Maxwell stress that serves to compress the DE under examination. According to Eq. 1, $\sigma_M$ in the case of an ideal DE is dependent on the dielectric constant of the DE ($\varepsilon$) and the applied electric field ($E$). Measured values of the real component of the complex dielectric constant ($\varepsilon'$) are provided as a function of frequency for both copolymer series in Fig. 4.10 and reveal several important features. The first is that an increase in DOP concentration significantly increases $\varepsilon'$ (in one case beyond 5.0), which is not surprising since the dielectric constant of pure DOP is 5.1. Whereas the VHB4910 acrylic elastomer exhibits a weak maximum in $\varepsilon'$ at 100 Hz and decreases slightly, but monotonically, at higher frequencies, some of the current ATPEGs in the MBM146 series display a minimum in $\varepsilon'$ at 100 Hz and then become almost independent of frequency at higher frequencies. In the MBM104 series, $\varepsilon'$ decreases with increasing frequency, but not to the same extent as the acrylic elastomer. The dependence of $\varepsilon'$ on copolymer concentration in both ATPEG series is provided at $10^3$ and $10^6$ Hz in Fig. 4.11 for completeness and confirms, as expected, that $\varepsilon'$ tends to increase with decreasing copolymer (and increasing DOP) concentration in both series and at both frequencies.
The results displayed in Figs. 4.10 and 4.11 confirm that the dielectric properties of ATPEGs are composition-tunable and that these materials are electrically stable over a broad frequency ranging spanning over four decades. Such stability is critically important for high-frequency applications such as those requiring flapping or rippling motion (e.g., a micro air or underwater vehicle). Figure 4.10 also shows that measured values of \( \varepsilon' \) for the SEBS75-45 TPEG and the VHB4910 acrylic elastomer are lower (by up to 100% and 30%, respectively) compared to those of the present ATPEGs. This difference suggests that the ATPEGs under investigation are more prone to respond to an applied electric field. Once a test specimen is mounted on a circular support and compliant electrodes are painted on both sides of the specimen, an electric field is applied, and the ensuing actuation is directly evaluated from the lateral (in-plane) change in active area, as discerned from analysis of real-time video footage.

Values of the maximum actuation strain, as well as the corresponding maximum transverse (thickness) strain, measured at failure for both ATPEG series at ambient temperature are displayed as a function of copolymer concentration in Fig. 4.12. Included in this figure for comparison are results reported\textsuperscript{[26]} for the SEBS75-45 TPEG and the VHB4910 acrylic elastomer without mechanical prestrain. At the lowest copolymer concentration investigated (45 wt%), the largest actuation strain occurs with the MBM146-45 formulation at \( \sim 115\% \), which is about 16\( \times \) that of the SEBS75-45 TPEG and 14\( \times \) that of the VHB4910 acrylic elastomer. Recall from Figs. 4.2 and 4.3 that this material possesses a spherical morphology with no evidence of the Mullins effect during strain cycling. In both ATPEG series, an increase in copolymer concentration promotes reductions in the maximum actuation and transverse strain due to a decrease in high-\( \varepsilon \) DOP and an increase in modulus.
The in-plane actuation strain is presented as a function of the nominal electric field (normalized with respect to initial film thickness) in Fig. 4.13 for all the ATPEGs examined here. Although both ATPEG series display a similar and conventional response to the applied electric field, Fig. 4.13a reveals an experimental phenomenon resulting from electromechanical stability\cite{41} that has not been previously reported: buckling. As the applied electric field is increased, a film thins so that the actual electric field is higher than the nominal electric field. This increase in electric field promotes further nonuniform thinning of the DE, followed by eventual failure. Before failure, the constraints imposed by the relatively stiff boundary of the active area, coupled with electromechanical instability, promotes out-of-plane deformation, as evidenced by the development of specimen buckling. Images acquired from the MBM146-65 formulation at three electric fields are numbered in Fig. 4.13a and show the formation of buckles, which is only observed in the case of the MBM146-based ATPEG series. We attribute this difference in electroactuation behavior to the lengths of the copolymer midblocks. Recall that the MBM104 copolymer possesses shorter midblocks that are extended upon microphase separation (before electroactuation). As the midblocks are stretched further at the onset of actuation, the film quickly stiffens to prevent the occurrence of instability.\cite{41} Failure at higher electric fields is a consequence of dielectric breakdown, the second mode of soft dielectric material failure according to Zhao and Suo.\cite{42} In the case of ATPEGs derived from the MBM146 copolymer, however, the midblocks are longer and can stretch more during actuation, thereby accommodating electromechanical instability. An implication of out-of-plane buckling is that the strain values (area and thickness) shown in Fig. 4.12 are underestimated significantly.
The results displayed in Fig. 4.13 permit direct comparison of the electric fields required for actuation. Maximum actuation (115% area strain) in the MBM146-45 system occurs at 26 kV/mm, whereas that in the MBM104-45 formulation (65% strain) requires a higher electric field (50 kV/mm). Under similar test conditions, the VHB4910 acrylic elastomer fails at 17-34 kV/mm after only ~7% actuation strain,[26] thus establishing the superior actuation performance of ATPEGs without mechanical prestrain. It is important to realize that the electric fields needed to actuate the ATPEGs in this work are generally lower than those required to actuate biaxially-prestrained DEs. While the precise reason for such improved actuation efficacy remains unclear, we contend that it is a consequence of the higher ε of the ATPEGs (due to the presence of DOP), in conjunction with the morphology-dependent mechanical properties of the materials. With regard to the latter consideration, a trend reported for DEs generated from SEBS-based TPEGs is that materials possessing the same (spherical) morphology exhibit overlapping trends in actuation strains and breakdown electric fields irrespective of copolymer molecular weight. In Fig. 4.14, the dielectric breakdown field is consistently higher in the MBM104 series and increases linearly with increasing copolymer concentration in both ATPEG series. Recall that, with the exception of the MBM104-45 formulation, all the ATPEGs in the MBM104 series possess cylindrical morphologies. A bcc spherical morphology can therefore be reasonably anticipated at copolymer concentrations below 45 wt%. According to SAXS (cf. Figs. 4.2 and 4.3), the spherical morphology does exist in the MBM146-45 system. Linear extrapolation of the two datasets displayed in Fig. 4.14 provides the point of intersection at ~33 wt% copolymer, which corresponds to about 9 and 14 vol% M in the MBM146 and MBM104 series,
respectively. At this concentration, a spherical morphology can be expected to form and, from the relationship established by Shankar et al.,[4] the actuation strains should be comparable. Difficulty associated with the preparation of such materials (which readily damage because they are excessively soft) has, however, thus far precluded experimental confirmation of this supposition.

Two additional electroactuation performance metrics introduced earlier in the Electroactuation Background and described in detail elsewhere[4,25] — the energy density (F) and electromechanical coupling efficiency (K²) — are shown as functions of copolymer concentration in Figs. 4.15a and 4.15b, respectively. In Fig. 4.15a, values of F determined from both ATPEG series are greater than those of the VHB4910 acrylic elastomer and SEBS75-45 TPEG. In addition, values of F calculated for the MBM146 series, while consistently lower than those from the MBM104 series, are nearly independent of copolymer concentration. This is not the case for K² shown in Fig. 4.15b. Here, values of K² calculated for the MBM146 series are significantly and generally larger than those from the MBM104 series. The maximum values of K² from each series are 77 and 64%, respectively, in marked contrast to 14% from the VHB4910 acrylic elastomer and 12% from the SEBS75-45 TPEG. It is important to recognize that the maximum efficiencies exhibited by the ATPEGs are higher than many DEs subjected to mechanical prestrain prior to electroactuation.[4] The current range of maximum efficiencies afforded by DEs (including those composed of VHB4910 or various TPEGs) are highlighted for completeness in Fig. 4.15b. The results obtained from the MBM104-based ATPEG series display two intriguing features: (i) K² increases sharply with decreasing copolymer concentration, and (ii) K² levels off at the value
of $K^2$ determined from the VHB4910 elastomer at high copolymer concentrations. Since $F$ and $K^2$ are calculated from transverse strains and, as explained earlier, these strains are underestimated due to the onset of electromechanical instability, the values obtained for these metrics are also anticipated to be largely underestimated. Comparison of these performance metrics with those of mammalian skeletal muscle in Table 1 confirm that the ATPEGs investigated here generally possess comparable, if not superior, electroactuation characteristics relative to muscle and are therefore suitable, on this basis, for (micro)robotic applications. In addition, these materials constitute ideal candidates as functional materials for large-scale touchscreen devices (e.g., televisions and computer screens) in which DEs requiring mechanical prestrain could be irreparably problematic over time.

4.5 Conclusions

Thermoplastic elastomer gels composed of MBM triblock copolymers differing in molecular weight and composition and a low-volatility, B-selective solvent consist of $M$ micelles (spherical or cylindrical) dispersed in a solvent-rich matrix. With the exception of one system (MBM104-45), all the MBM104 formulations examined here possess the hexagonally-packed cylindrical morphology, according to SAXS analysis. In marked contrast, the only morphology that could be conclusively assigned on the basis of SAXS data in the MBM146 series is spherical on a bcc lattice (for MBM146-45). Mechanical property analysis reveals that an increase in copolymer concentration promotes concurrent increases in the ultimate stress at failure and the tensile modulus due to a corresponding increase in the
fraction of the glassy M endblocks. The Mullins effect, described as stress softening upon cyclic loading and unloading, is observed in the MBM104 ATPEG series, but not to the same extent in the MBM146 series. The existence of dispersed cylinders that microbuckle under stress are presumed to be responsible for this behavior. Due to its spherical morphology, however, the MBM146-45 system displays almost no evidence of this effect. This observation strongly suggests that, within the present ATPEG series, the dispersed elements comprising the copolymer nanostructure must be rigid (glassy) and irreversibly deform under an applied load for the Mullins effect to manifest. As expected, the mechanical properties of ATPEGs directly influence the electroactuation properties achieved, with stiffer materials exhibiting smaller actuation strains. Due to their relatively high dielectric constants, the present ATPEGs undergo actuation without any mechanical prestrain and at relatively low electric fields compared to other DEs. Measured actuation strains are sensitive to both copolymer nanostructure and tensile modulus. Electromechanical instability resulting in out-of-plane actuation manifests as buckles and develops in the MBM146 series due most likely to the longer B midblock than in the MBM104 series. Cylindrical copolymer morphologies exhibit higher breakdown electric fields than spherical morphologies, thus confirming that the copolymer nanostructure directly influences the development of electromechanical properties. Maximum values of actuation (area) strain, energy density and electromechanical coupling efficiency — ~110%, ~50 kJ/m³ and ~80%, respectively — match or exceed the electromechanical attributes of skeletal muscle (cf. Table 1), thereby making ATPEGs suitable for a wide variety of biomimetic applications, as well as advanced engineering and biomedical technologies.
4.6 Acknowledgments

This work was supported by the National Science Foundation. We thank Dr. Arjun Krishnan for valuable discussions.
Table 4.1 Comparison of electroactuation performance metrics for various systems with no mechanical prestrain.

<table>
<thead>
<tr>
<th>Property</th>
<th>Mammalian skeletal muscle$^{[17]}$</th>
<th>VHB4910 acrylic elastomer$^{[26]}$</th>
<th>SEBS75 TPEGs$^{[26]}$</th>
<th>ATPEGs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Maximum</td>
<td>Maximum</td>
<td>Maximum$^a$</td>
</tr>
<tr>
<td>Area actuation strain (%)</td>
<td>20</td>
<td>&gt; 40</td>
<td>8</td>
<td>3-19</td>
</tr>
<tr>
<td>Energy density (kJ/m$^3$)</td>
<td>8</td>
<td>40</td>
<td>6</td>
<td>1-26</td>
</tr>
<tr>
<td>Coupling efficiency (%)</td>
<td>—</td>
<td>40</td>
<td>14</td>
<td>6-29</td>
</tr>
</tbody>
</table>

$^a$ Since the properties of TPEGs and ATPEGs are sensitive to copolymer concentration, a range is provided.

Table 4.2 Characteristics of the two MBM triblock copolymers used in this study.$^a$

<table>
<thead>
<tr>
<th>Copolymer designation</th>
<th>Composition (wt% M)</th>
<th>Number-average molecular weight (kDa)</th>
<th>Polydispersity index</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBM104</td>
<td>50.0</td>
<td>104</td>
<td>1.56</td>
<td>Arkema, Inc.</td>
</tr>
<tr>
<td>MBM146</td>
<td>31.3</td>
<td>146</td>
<td>1.04</td>
<td>Kuraray America</td>
</tr>
</tbody>
</table>

$^a$ The molecular weight values listed here were measured by size exclusion chromatography (unlike those provided by the manufacturers in ref. 29).
Table 4.3 Thermal properties of the MBM104 and MBM146 ATPEGs according to DSC analysis.

<table>
<thead>
<tr>
<th>ATPEG Series</th>
<th>Copolymer concentration (wt%)</th>
<th>Endblock $T_g$(^a) (°C)</th>
<th>Midblock $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBM104</td>
<td>100</td>
<td>106.2</td>
<td>-46.5</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>66.1</td>
<td>-72.7</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>59.0</td>
<td>-73.9</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>56.4</td>
<td>-74.5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50.3</td>
<td>-76.3</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>49.7</td>
<td>-77.7</td>
</tr>
<tr>
<td>MBM146</td>
<td>100</td>
<td>120.6</td>
<td>-41.7</td>
</tr>
<tr>
<td></td>
<td>65</td>
<td>109.6</td>
<td>-72.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>79.1</td>
<td>-76.9</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>80.8</td>
<td>-75.4</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>79.0</td>
<td>-76.5</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>73.5</td>
<td>-77.5</td>
</tr>
</tbody>
</table>

\(^a\) Unlike the lower $T_g$, the upper $T_g$ in many of the specimens tested was broad.
Table 4.4 Morphological details extracted from the SAXS patterns acquired from the MBM104 and MBM146 ATPEGs at 135°C (in the melt) and 35°C (with glassy endblocks).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>ATPEG Series</th>
<th>Copolymer concentration (wt%)</th>
<th>$2\pi/q^a$ (nm)</th>
<th>Peak ratios</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>MBM104</td>
<td>100</td>
<td>34.9</td>
<td>1:1.97:2.96</td>
<td>Lamellar</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>34.8</td>
<td>1:1.71:1.99:2.66</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>34.9</td>
<td>1:1.97:2.66</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>34.7</td>
<td>1:1.99:2.65</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>35.9</td>
<td>1:1.98:2.84:3.30</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>35.6</td>
<td>1:2.02</td>
<td>Uncertain</td>
</tr>
<tr>
<td>35</td>
<td>MBM104</td>
<td>100</td>
<td>34.9</td>
<td>1:1.97:2.96</td>
<td>Lamellar</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>34.7</td>
<td>1:1.74:1.99:2.68:3.46</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>33.3</td>
<td>1:1.73:1.97:2.64</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>35.4</td>
<td>1:1.99:2.66</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>36.5</td>
<td>1:1.75:2.02:2.62</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>37.6</td>
<td>1:2.66</td>
<td>Uncertain</td>
</tr>
<tr>
<td>135</td>
<td>MBM146</td>
<td>100</td>
<td>35.7</td>
<td>1:1.73:2.65:3.02</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>35.7</td>
<td>1:1.71:2.46</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>35.8</td>
<td>1:1.72:2.45</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>34.6</td>
<td>1:1.70:2.43</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>34.4</td>
<td>1:1.70:2.46</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>33.3</td>
<td>1:1.42:1.75:2.25:2.44</td>
<td>Spherical</td>
</tr>
<tr>
<td>35</td>
<td>MBM146</td>
<td>100</td>
<td>35.2</td>
<td>1:1.71:2.01:2.65</td>
<td>Cylindrical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>35.0</td>
<td>1:2.02:2.45</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>34.9</td>
<td>1:1.70:2.43</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55</td>
<td>34.9</td>
<td>1:1.63:2.43</td>
<td>Uncertain</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>33.9</td>
<td>1:1.63:1.99:2.44</td>
<td>Uncertain</td>
</tr>
</tbody>
</table>
Table 4.4 continued

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$q^*$ denotes the wave vector of the principal scattering peak.

Figure 4.1 Schematic illustration of the general actuation mechanism exhibited by DEs. During actuation, electrostatic attraction of the oppositely charged compliant electrodes on each side of the DE film, coupled with repulsion of like charges along each electrode, generates a compressive stress referred to as the Maxwell stress (the magnitude of which is given by Eq. 1 for an ideal DE) within the active area of the electrodes.
Figure 4.2 SAXS profiles acquired for the (a) MBM104 and (b) MBM146 ATPEG series at 135°C (with the exception of the MBM104-45 formulation, which was measured at 90°C to keep it below its order-disorder transition at ~120°C, according to dynamic rheology). Scattering peaks are identified by open arrowheads, and copolymer concentrations (in wt%) are labeled.
Figure 4.3 SAXS profiles acquired for the (a) MBM104 and (b) MBM146 ATPEG series at 35°C (below $T_g$ of the M endblocks). Scattering peaks are annotated in the same fashion described in the caption of Fig. 4.2.
Figure 4.4 Nominal (engineering) stress displayed as a function of strain for the (a) MBM146 and (b) MBM104 ATPEGs at ambient temperature. Solid lines serve to connect the data (not all data points are shown), and copolymer concentrations (in wt%) are labeled.
Figure 4.5 (a) Tensile moduli measured at ambient temperature from uniaxial stress-strain curves and presented as a function of copolymer concentration for the MBM104 (O) and MBM146 (Δ) ATPEG series. (b) Values of the stress (open symbols) and strain (filled symbols) evaluated at failure in both copolymer series: MBM104 (diamonds) and MBM146 (squares). Solid lines are straight lines through the data and serve as guides for the eye, and error bars correspond to the standard error in the data.
Figure 4.6 Cyclic tensile stress-strain curves obtained by loading and unloading (a,b) MBM146 and (c,d) MBM104 formulations with (a,c) 45 and (b,d) 60 wt% copolymer. For clarity, data collected from only the 1st (O), 2nd (●) and 30th (△) cycles are displayed. Hysteresis is evident from (i) the development of stress softening (the reduction in stress at the maximum applied strain), (ii) the area within loading-unloading loops and (iii) the non-recoverable strain, or set (the shift in curves along the strain axis upon cycling).
Figure 4.7 Stress softening evaluated from cyclic tensile stress-strain curves as the maximum stress of each cycle ($\sigma_n$) normalized by that of the first cycle ($\sigma_1$) and presented as a function of cycle number (n) for the MBM146 and MBM104 ATPEG series (solid and dashed lines, respectively). The curves are shifted vertically by one unit for clarity, and the copolymer concentrations (in wt%) are labeled.
Figure 4.8 Dependence of non-recoverable strain (set) measured at the end of 30 loading-unloading cycles up to 100% strain on copolymer concentration for the MBM104 (O) and MBM146 (△) ATPEG series. Solid lines are linear fits to the data and serve as guides for the eye.
Figure 4.9 Cyclic tensile loading-unloading curves measured between stress points as the upper stress limit is progressively increased after completing 1 cycle for the (a) MBM146 and (b) MBM104 ATPEGs with 60 wt% copolymer. Subsequent cycles are differentiated by alternating solid and dotted lines. Corresponding data obtained from tensile tests conducted to failure (cf. Fig. 4.4) are included.
Figure 4.10 Frequency dependence of the real dielectric constant ($\varepsilon'$) measured at three different copolymer concentrations (in wt%) in the (a) MBM146 and (b) MBM104 ATPEG series: 45 (O), 55 (△) and 65 (○). Other ATPEGs not shown (for clarity) exhibit similar trends. Results from the VHB4910 acrylic elastomer (●) and SEBS75-45 TPEG (■) are included for comparison, and the dashed lines serve to connect the data.
Figure 4.11 Dependence of $\varepsilon'$ on copolymer concentration in the MBM104 (circles, solid lines) and MBM146 (triangles, dashed lines) ATPEG series evaluated at $10^3$ (open symbols) and $10^6$ (filled symbols) Hz. The solid and dashed lines serve to connect the data.
Figure 4.12 Maximum electroactuation-induced area (open symbols) and thickness (filled symbols) strains presented as functions of copolymer concentration for MBM104 (circles) and MBM146 (triangles) ATPEGs without mechanical prestrain conditions. Error bars correspond to the standard error in the data. The corresponding actuation metrics of the SEBS75-45 TPEG (diamonds) are included for comparison, as are those of the VHB4910 acrylic elastomer likewise actuated without prestrain (thick and thin dashed lines denote area and thickness strains, respectively).
Figure 4.13 Area actuation strain displayed as a function of applied electric field for the (a) MBM146 and (b) MBM104 ATPEG series. Copolymer concentrations (in wt%) are labeled. Dashed lines serve as guides for the eye, while the solid lines are linear fits to the electromechanical (pull-in) instability regime. The images show the active (electrode) area in the MBM146-65 formulation in (a) at electric fields that are identified (■) and numbered.
Figure 4.14 Maximum (breakdown) electric field displayed as a function of copolymer concentration for the MBM104 (O) and MBM146 (Δ) ATPEG series. The solid lines are linear regressions to the data and are provided as guides for the eye.
Figure 4.15 Dependence of (a) energy density ($F$) and (b) electromechanical coupling efficiency ($K^2$) on copolymer concentration for MBM104 (○) and MBM146 (△) ATPEGs subjected to electroactuation without mechanical prestrain. Error bars correspond to the standard error in the data. Corresponding results obtained under similar test conditions from the SEBS75-45 TPEG (◇) and VHB4910 acrylic elastomer (dashed line) are included for comparison. Solid lines serve to connect the data.
4.7 References


5 Exceptional Versatility of Solvated Block Copolymer/Ionomer Networks as Electroactive Polymers

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Responsive materials possess properties that change abruptly when exposed to an external stimulus, and electroactive polymers constitute examples of robust, lightweight materials that change shape upon electrical actuation. We demonstrate that solvated block copolymer networks afford tremendous versatility in designing electronic and ionic electroactive polymers. As dielectric elastomers, styrenic block copolymer systems attain extraordinary actuation strains approaching 300%, along with high electromechanical coupling efficiencies. Changing the solvent improves the blocking stress and yields exceptionally high energy densities, while providing a unique opportunity for mechanical impedance matching and control of shape recovery kinetics, as well as mode of deformation. Dielectric elastomers composed of acrylic copolymers actuate beyond 100% in-plane strain without any prestrain, whereas block ionomer networks swollen with ionic solutions yield ionic polymer-metal composites, which actuate by bending. Selective solvation of block copolymer networks represents an effective and largely unexplored means by which to tune

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the function and properties of electroactive polymers through systematic manipulation of copolymer and solvent attributes.

Responsive, smart or otherwise programmable materials undergo a substantial, often reversible, change in one or more properties upon application of, or variation in, an external stimulus. An abrupt variation in size or shape, for instance, can be used to extract mechanical work and thus impart a force or motion. Stimuli capable of inducing size/shape transformations in soft materials such as polymers include changes either in the chemical environment — e.g., pH \(^1\) or ionic \(^2\) concentrations — or in physical conditions — e.g., temperature \(^3\) or electromagnetic radiation.\(^4\)-\(^7\) Of these, electrical actuation has sparked considerable interest due to the diverse spectrum of science fiction-like technologies,\(^8\),\(^9\) ranging from (micro)robotics, mechatronics and large-scale touch screens to functional prosthetics and tactile sensors, that can be realized. Being mechanically robust, lightweight, relatively inexpensive and highly processable,\(^10\) electroactive polymers are broadly classified as electronic or ionic, depending on the mechanism by which they activate in the presence of an electric field.\(^11\)-\(^13\) Electronic systems undergo dimensional change due to a field-induced dielectric response, which can be described as electrostrictive or electrostatic. Electrostriction occurs when electric polarization changes with mechanical strain in such macromolecules as ferroelectric poly(vinylidene fluoride) and its co/terpolymers,\(^5\),\(^14\),\(^15\) which go through a phase transition upon application of an electric field. Examples of electrostatic polymers, on the other hand, are thin dielectric elastomer (DE) membranes that compress transversely and expand laterally due to field-induced attraction of oppositely charged surface electrodes.\(^5\),\(^16\) Lastly, ionic systems rely on ion transport in a polar solvent to promote shape change and
include carbon nanotubes and ionic polymer-metal composites (IPMCs).

Electroactive polymers designed for cyclic motion (e.g., flapping to emulate a wing) require high-fidelity shape recovery with minimal strain hysteresis. Polymer elasticity, in turn, depends on the existence of a cross-linked network that is sufficiently robust to (i) endure moderate to high strain levels without rupturing and then (ii) restore a strained specimen to its original dimensions upon removal of an applied stress. For this reason, elastomers are ideally suited as DE membranes, although additional considerations must be addressed to ensure that the network overcomes electromechanical instability to attain large actuation strains. Networks in polymers can be generated by chemical or physical means, with the former introducing covalent bonds as permanent cross-link sites. Alternatively, macromolecules such as linear triblock copolymers that behave as thermoplastic elastomers microphase-separate into nanostructures wherein rubbery midblocks are physically cross-linked by, and thus connect, glassy microdomains. The mechanical properties of the resulting thermoreversible network can be finely adjusted by adding a low-volatility, midblock-selective solvent. Incorporation of mineral oil into poly[styrene-\(b\)-(ethylene-co-butylene)-\(b\)-styrene] (SEBS) triblock copolymers, for instance, yields DE membranes that exhibit high strain levels (>200%) and electromechanical property attributes comparable to human muscle at relatively low electric fields (as low as \(~30\ V/\mu m\)) relative to other DE materials. Here, we demonstrate that this paradigm based on selectively-solvated block copolymers is, unlike other electroactive polymers, remarkably versatile and capable of yielding not only DE membranes but also IPMCs with promising characteristics.

The electromechanical properties of the DE membranes investigated in this study have
been measured using a circular test configuration\textsuperscript{5,16} to permit quantitative comparison with other DEs. Compliant electrodes (Ag grease; Chemtronics Circuit Works, Kennesaw, GA) are applied as active areas on both sides of the DE membrane prior to actuation, which is induced using a manual voltage trigger and followed by frame-by-frame analysis of real-time video footage. In this arrangement, a Maxwell stress develops upon actuation and acts normal to the DE surface, thereby compressing the membrane while stretching it laterally. The strain induced in response to application of an electric field is discerned by measuring the active area before and after actuation and then calculating the in-plane area strain ($\varepsilon$). For consistency with prior studies and unless otherwise stated, electrical actuation strains are reported here on an area basis. Alternatively, the radial displacement, or stretch, associated with actuation ($\lambda$) is defined as $(r_o + \Delta r)/r_o$, where $r_o$ is the initial radius of the active area and $\Delta r$ is the actuation-induced change in radius. From this, $\lambda$ can be determined from $(1 + \varepsilon)^{1/2}$, assuming that actuation occurs isotropically. In the first case considered here, we have used mineral oil (Witco Hydrobrite 380; Crompton Corp., Petrolia, PA) to swell two styrenic thermoplastic elastomers (Kuraray America, Inc., Houston, TX): poly[styrene-\textit{b}-(ethylene-alt-propylene)-\textit{b}-styrene] (SEPS: 306 kDa, 35 wt% S) and poly[styrene-\textit{b}-(ethylene-co-\{ethylene-alt-propylene\})-\textit{b}-styrene] (SEEPS: 195 kDa, 32 wt% S). Maximum actuation strains measured after 300% equibiaxial prestrain (to reduce specimen thickness and lower the voltage required to induce actuation) are presented in Fig. 5.1A and reveal that both systems can exceed 200% strain, with the SEPS system approaching 300% strain, upon actuation without the use of specialty electrodes.\textsuperscript{23} Over the composition range explored, the achievable strain is tunable with respect to copolymer concentration, but is always greater
than ~100%. For comparison, the maximum strain reported\textsuperscript{5} for a benchmark acrylic adhesive (VHB 4910: 3M Co., Minneapolis, MN) is 158% under identical conditions.

A transmission electron microscopy (TEM) image of SEPS modified with 70 wt% oil, cryoultramicrotomed at −100°C, selectively stained with RuO\textsubscript{4}(aq) and imaged with a Tecnai T20 microscope operated at 200 keV is included in the inset of Fig. 5.1A and confirms the existence of a dispersed micellar morphology wherein glassy spherical micelles (stained) stabilize the oil-swollen rubbery network. At the oil concentrations examined here (70 to 95 wt%), both copolymers retain similar micellar morphologies. The upper limit on the oil level is set by the critical gel concentration, which identifies the lowest copolymer concentration at which a network forms by copolymer midblocks that connect, or bridge, adjacent micelles.\textsuperscript{24} At large strains, these molecular bridges are primarily responsible for storing mechanical energy, and the electromechanical coupling efficiency (K\textsuperscript{2}) constitutes a measure of that stored energy relative to the electrical energy used to induce actuation. Values of K\textsuperscript{2} in Fig. 5.1B confirm that the swollen SEPS and SEEPS copolymers are consistently greater than ~75%, achieving a maximum of 93%, in contrast to VHB 4910 for which K\textsuperscript{2} ≈ 85%. Another electromechanical property evaluated here is the energy density (\hat{E}), which quantifies the ability of an actuator to perform work.\textsuperscript{5} Figure 5.1C shows that \hat{E} increases monotonically for the two swollen copolymers examined here. Maximum values discerned at 70 wt% oil surpass 1.5 MJ/m\textsuperscript{3}, which exceeds comparable values reported\textsuperscript{16} earlier for DEs composed of solvated SEBS copolymers. While this value is higher than that afforded by most DEs and provides a clear indication that the present DEs can meet the actuation demands of a wide variety of electroresponsive applications, it remains markedly less than the 3.4 MJ/m\textsuperscript{3}
ascertained\textsuperscript{5} for VHB 4910. The actuation characteristics displayed in Fig. 5.1 for swollen SEPS and SEEPS DEs nonetheless establish that a small change in copolymer chemistry and accompanying physical attributes can have a significant impact on electromechanical properties. More profound property changes can be achieved by using different midblock-selective solvents.

In the second case of this DE study, a hydrocarbon tackifying resin, frequently added to polymers in the formulation of adhesives,\textsuperscript{25} is employed as the midblock-selective solvent. Incorporation of the resin (Escorez 5380: 190 Da, ExxonMobil, Houston, TX), which consists of hydrogenated ring moieties and possesses a glass transition temperature of 30°C, into a SEBS triblock copolymer boosts the blocking stress (defined in terms of the force required to return a fully energized actuator to zero displacement and providing a measure of the ability of a DE to move an object) to beyond 700 kPa, which exceeds that of mammalian skeletal muscle\textsuperscript{26} (\textasciitilde550 kPa). This resin also serves to increase $\hat{E}$ of the DE to beyond 8 MJ/m\textsuperscript{3}, which is close to that of ferroelectric polymers.\textsuperscript{12} More intriguing, however, is the observation that resin-containing copolymers do not immediately actuate fully, nor do they abruptly return to their original dimensions upon electrical discharge, due to the high viscosity of the resin, which slows down the deformation and elastic recovery of the network. According to the voltage-jump measurements presented in Fig. 5.2, the actuation-induced strain in a SEBS copolymer (265 kDa, 33 wt% S) solvated with 70 wt% oil and subjected to an electric field of 100 V/\textmu m increases rapidly to about 1 s (high voltage is reached in \textasciitilde10 ms) and then slows down over the course of the experiment (or, in some cases, until the material fails due to continued thinning). Conversely, actuation of the same copolymer
solvated with the same concentration of resin and subjected to both low and high fields results in strain responses that start slowly and then increase to field-dependent extents thereafter. As shown in this figure, intermediate strain behavior can be controllably achieved by mixing resin with oil to form ternary blends exhibiting time-composition equivalence. Unlike conventional DEs capable of rapid actuation and shape recovery upon electrical discharge, these systems can be programmed by judicious choices of co-solvent composition and field strength to achieve a target actuation (or recovery) level over a predetermined time interval (cf. Fig. 5.2), which makes them suitable for timed switches. The standard linear solid (Zener) model is capable of addressing viscoelastic creep and permits the compliance $J(t) = \varepsilon(t)/\sigma_0$, where $\varepsilon(t)$ is the time-dependent strain resulting from an instantaneous stress, to be written in terms of $n$ elements as $J_0 + \sum_{i=1}^{n} J_i [1 - \exp(-t/\tau_i)]$. Here, $J_i$ and $\tau_i$ denote the compliance and relaxation time of the $i$th element. Since $\sigma_0$ is constant, this functional expression can likewise be used to describe $\varepsilon(t)$, as demonstrated in Fig. 5.2. The favorable agreement evident in this figure indicates that the time-dependent change in strain due to electromechanical actuation induced by a voltage jump (and the onset of the corresponding Maxwell stress) is fundamentally equivalent to mechanical creep. While the tackifying resin permits formulation of DEs with programmable timed responses, mineral oil mixed with a natural midblock-selective solvent such as soybean oil, often used in inks, paints and biodiesel, can likewise be used to swell the SEPS copolymer discussed earlier in Fig. 5.1 to yield biosustainable DEs exhibiting actuation strains beyond 100% after 300% equibiaxial prestrain.
Thus far, only styrenic copolymers have been explicitly considered here. To confirm the generality of the design principle by which DEs with tailorable properties can be produced from selectively-solvated triblock copolymers, we next consider two grades of an acrylic thermoplastic elastomer, poly(methyl methacrylate-\(b\)-n-butyl acrylate-\(b\)-methyl methacrylate) (MBM1: 101 kDa, 31.3 wt% M, Kuraray America, Inc.; MBM2: 47 kDa, 50.0 wt% M, Arkema, Inc., King of Prussia, PA) swollen with dioctyl phthalate (DOP). Although DEs prepared from these solvated MBM copolymers are not as mechanically robust as the styrenic ones, they afford a highly desirable feature: they do not require prestrain to display significant electrical actuation. As mentioned earlier, prestrain is routinely applied to DEs to reduce specimen thickness and, thus, the voltage required for actuation. The level of prestrain, often applied in uniform biaxial fashion, is sensitive to the properties of the DE under consideration and requires the use of hardware, which adds to device weight. Moreover, when kept under an applied load for an extended period of time, macromolecules undergo stress relaxation, which can have a deleterious effect on actuator performance. Without prestrain, however, most DEs fail to perform satisfactorily at viable electric fields (<300 V/\(\mu\)m). While the VHB 4910 acrylic adhesive, when subjected to a 300% equibiaxial prestrain, exhibits >150% strain upon actuation,\(^5\) actuation without prestrain results in a dramatically lower response.\(^{29}\) Ha et al.\(^{30}\) have demonstrated that prestraining VHB 4910 modified with a reactive diacrylate, followed by chemical cross-linking of the diacrylate and subsequent prestrain release, yields a locked-in interpenetrating network that largely retains its prestrained state and exhibits actuation levels approaching 300%. Without any prestrain treatment or conditioning, the DOP-solvated MBM1 copolymer is capable of achieving
110% strain (cf. Fig. 5.3A) and 78% coupling efficiency upon electrical actuation. This makes the MBM/DOP system an ideal candidate for large touch screens and tactile sensors.

Because no prestrain is required for electrical actuation at any time during specimen preparation, these DEs can be compared to predictions from the recent theoretical formalism proposed by Zhao and Suo. Within the context of their framework, the electromechanical stress-strain behavior is expressed in terms of voltage-stretch (Φ−λ) curves. Electromechanical Φ−λ curves measured from the MBM1/DOP series at three of the copolymer concentrations in Fig. 5.3A are presented in Fig. 5.3B and reveal several important comparative features. The first is that Φ(λ) monotonically increases and never exhibits a local maximum, contrary to other DE materials such as the VHB 4910 adhesive (which is predicted to exhibit a maximum at $\lambda \approx 1.26$). Absence of this maximum is attributed to network stiffening at low strains. A second feature is that, while values of the dielectric breakdown voltage ($\Phi_B$) vary with copolymer concentration, $\Phi_B(\lambda)$ can be accurately fitted to a curve of the form $\Phi_0 + H\lambda^{-2}E_B$, where $\Phi_0$ is a constant that relates to composition effects, H is the initial specimen thickness and $E_B$ is the nominal breakdown field measured upon actuation failure at each copolymer concentration. This relationship confirms that $\Phi_B \sim \lambda^{-2}$, from which it follows that $E_B$ is largely independent of strain, in agreement with theoretical expectations. Lastly, the shapes of the curves in Fig. 5.3B closely resemble those predicted for DEs swollen to the same extent, but varying in chain length. Our results are interpreted to indicate that equivalent electromechanical curves can be
experimentally obtained by conversely swelling a single DE of constant chain length to different extents.

The remaining case considered here further extends the selectively-solvated block copolymer paradigm developed for DEs to multiblock ionomers and the preparation of IPMCs. With this objective in mind, the ideal design (cf. Fig. 5.4A) is envisaged to consist of a midblock that is made polar through, for instance, sulfonation and consequently solvated. The glassy endblocks would still perform their function of serving as physical cross-links to stabilize the selectively-swollen copolymer network. This approach differs markedly from previous studies\textsuperscript{31} of IPMCs prepared from block ionomers wherein styrenic endblocks have been sulfonated. In such cases, endblock sulfonation/swelling compromises the ability of the macromolecules to form a mechanically robust physical network. Another benefit of the present design is that the degree of midblock sulfonation can be chemically varied so as to tune the extent of solvent uptake, which constitutes a crucial role in the mechanism of IPMC actuation. Recall that, unlike electroactive polymers such as DEs, IPMC actuation relies on potential-driven ion transport in a solvent medium. Nafion\textsuperscript{®}, a sulfonated ionomer often employed in proton exchange membrane fuel cells, is routinely used in the preparation of IPMCs, but only exhibits a water uptake level of about 30 wt\%.\textsuperscript{32} In contrast, a poly\[t\text{-butyl styrene-}b\text{-}(ethylene-}alt\text{-propylene)-}b\text{-}(styrene-}co\text{-styrenesulfonate)-}b\text{-}(ethylene-}alt\text{-propylene)-}b\text{-}t\text{-butyl styrene}\] (tbSEPsSEPtbS: 78 kDa, 38 wt% tbS, 26 wt% EP (before sulfonation), 57 mol% styrene sulfonation, Kraton Polymers, Houston, TX) pentablock ionomer can absorb up to \(~250\ wt%\) water (\(~450\ wt%\) glycerol) while remaining handleable.
Cast films of the pentablock ionomer are plated on both sides, first with Pt and then Ag, and subsequently exposed to an ionic solution to introduce mobile Li$^+$ cations into water-swollen regions containing immobilized sulfonic acid anions. Details of the plating will be provided in a forthcoming publication. While these IPMCs can be operated with water as the polar solvent, we have elected to replace the water with glycerol to avoid premature solvent evaporation, as well as water electrolysis at 1.23 V. Application of a voltage across the IPMC results in the diffusion of cations through well-defined nanoscale channels to the cathode. This migration is accompanied by an electro-osmotic force that further swells the cathode side of the IPMC while depleting the anode side of solvent, thereby resulting in a bending motion, as evidenced by the overlaid series of optical images shown in Fig. 5.4B. Due to the large electrical actuation achieved, the bending response is presented in terms of L/R, where L is the length of the IPMC and R is the radius of curvature of the IPMC upon actuation. Actuation kinetics are provided in Fig. 5.4C for the IPMCs prepared here at different applied voltages and reveal that the extent of actuation increases with increasing actuation time to saturation. For comparison, data reported for IPMCs produced with Nafion® are included in Fig. 5.4C. It is important to note that the Nafion®-based IPMCs exhibit a maximum deflection and then back-relax (in some cases beyond the zero point), whereas the present IPMCs retain their full electrical actuation until the voltage is removed. The results presented here taken together confirm that the use of selectively-solvated block copolymers/ ionomers affords a robust, versatile, and largely untapped means by which to generate, in systematic fashion, high-performance electroactive polymers with variable
actuation mechanisms and broadly tunable properties that depend on both copolymer and solvent attributes.

Acknowledgments

This work was supported by the National Science Foundation, the U. S. Department of Commerce through the National Textiles Center and Eaton Corporation.
Figure 5.1 Electromechanical properties — (A) maximum actuation strain, (B) coupling efficiency ($K^2$) and (C) energy density ($\hat{E}$) — of oil-solvated SEPS (red) and SEEPS (blue) triblock copolymers (of constant initial thickness before equibiaxial prestrain) upon electrical actuation (cf. the schematic illustration). Included in (A) are solvated SEBS copolymers varying in initial thickness$^{16}$ (green) and silicone elastomers$^5$ ($\Delta$), as well as the acrylic adhesive VHB-4910 reported alone$^5$ (O) and in an interpenetrating network$^{29}$ (□). The TEM image provided in (A) is obtained from a 30/70 w/w SEPS/oil blend and displays the micellar morphology responsible for network formation (the styrenic units are selectively stained and appear dark). The solid lines serve to connect the data. The colored area in (A) shows our region of high-performance, low-field DEs, and the dashed line in (B) identifies an efficiency of 90%.
Figure 5.2 Actuation kinetics of dielectric materials composed of a SEBS copolymer solvated with 70 wt% oil, tackifying resin or a mixture thereof (labeled in terms of wt% resin) after a voltage jump to one of two electric fields (color-coded). The solid lines represent data regressions of a two-element standard linear solid (Zener) model, as described in the text.
Figure 5.3 (A) Maximum actuation strain without prestrain presented as a function of copolymer concentration illustrating the variation achievable by changing the copolymer/solvent pair. Systems include DOP-solvated MBM1 and MBM2 triblock copolymers (labeled) and, for comparison, oil-solvated SEBS copolymers\textsuperscript{28} (O). Values measured for the VHB 4910 and 4905 adhesives are identified by dashed and dotted lines, respectively, whereas solid lines connect the data. (B) Electromechanical $\Phi$–$\lambda$ measurements
for MBM1/DOP systems differing in copolymer concentration (labeled, in wt% MBM1). Solid lines serve to connect the data. Included in (B) are dielectric breakdown voltages (◇) connected by an equation of the form $\Phi_B = \Phi_0 + H\lambda^{-2}E_B$ (dashed line).

Figure 5.4 (A) Schematic diagram (not drawn to scale) of an idealized IPMC produced from a midblock-sulfonated/solvated pentablock copolymer before actuation. On the basis of the present materials design, glassy micellar cores (depicted as spherical for simplicity) surrounded by a rubbery shell reside in a matrix composed of styrenesulfonic acid chains (red dots denote immobilized anions) swollen with a polar solvent and mobile cations (+). (B) Overlaid snapshots of the experimental IPMC as it responds to an applied voltage (7 V) at 5 min time intervals. (C) actuation kinetics of IPMCs prepared with glycerol as solvent. Included here are the solvated copolymers prepared in this study (colored symbols, solid lines, labeled with the cation and applied voltage) and Nafion®-based systems reported elsewhere (open symbols, dotted lines, labeled with the cation, at 2 V). Background colors indicate the electrode toward which the IPMC bends: cathode (tan) and anode (green).
References


(19) *Polymer Gels and Networks* (Eds: Y. Osada, A. Khokhlov), Marcel Dekker, New York **2002**.


6 Enhanced Biomimetic Performance of Ionic Polymer-Metal Composite Actuators Prepared with Nanostructured Block Ionomers

Ionic polymer-metal composites (IPMCs) represent an important class of stimuli-responsive polymers that are capable of bending upon application of an electric potential. Conventional IPMCs, prepared with Nafion® and related polyelectrolytes, often suffer from processing challenges, relatively low actuation levels and back relaxation during actuation. In this study, we examine and compare the effects of fabrication and solvent on the actuation behavior of a block ionomer with a sulfonated midblock and glassy endblocks that are capable of self-organizing and thus stabilizing a molecular network in the presence of a polar solvent. Unlike Nafion®, this material can be readily dissolved and cast from solution to yield films that vary in thickness and exhibit enormous solvent uptake. Cycling the initial chemical deposition of Pt on the surfaces of swollen films (the compositing process) increases the extent to which the electrodes penetrate the films, thereby improving contact along the polymer/electrode interface. The maximum bending actuation measured from IPMCs prepared with different solvents is at least comparable, but is often superior, to that reported for conventional IPMCs, without evidence of back relaxation. An unexpected characteristic observed here is that the actuation direction can be solvent-regulated. Our results confirm that this block ionomer constitutes an attractive alternative for use in IPMCs and their associated applications.

Electroactive polymers (EAPs) constitute a rapidly growing genre in the blossoming field of stimuli-responsive polymers[1] and afford a wide variety of important material-related
advantages over their inorganic counterparts. Some of these benefits include light weight, low cost, mechanical robustness, facile processability, and straightforward scalability. Macromolecules classified as EAPs are further categorized according to the mechanism by which they undergo actuation upon application of an electrical potential. In the case of electronic EAPs, the mode of actuation depends on whether an applied field either promotes attraction of compliant, oppositely-charged surface electrodes to compress a low-modulus polymer (the electrostatic mechanism) or induces a change in molecular polarization and, hence, lattice dimensions of a semi-crystalline polymer (the electrostrictive mechanism). Examples of electrostatic and electrostrictive EAPs are dielectric elastomers and ferroelectric polymers, respectively. Actuation can likewise occur by an ionic mechanism wherein ionic species migrate from one electrode to another and, by doing so, induce a change in the size and/or shape of a solvated polymer. Although systems developed with carbon nanotubes fall into this category, we only consider further here ionic polymer-metal composites (IPMCs), wherein ion transport is accompanied by solvent diffusion and sufficient nonuniform polymer swelling to trigger a bending motion. Due to their inherent similarity to biological muscle, IPMCs are often referred to as artificial muscle, and their electrical actuation is considered biomimetic. They can be used in motion-control devices (e.g., micropumps, grippers, camera apertures, and catheters) and are alternatively suitable for energy harvesting and vibration sensing. Since the transport of ionic species necessitates a solvent-swollen hydrophilic polymer, most conventional IPMCs consist of a polyelectrolyte such as Nafion®, a sulfonated fluorocarbon-based copolymer. In this study,
we report how, with appropriate preparation, a block ionomer can provide comparable, if not superior, electroactuation performance.

Block ionomers derive from block copolymers, which have become increasingly ubiquitous in fundamental and technological endeavors due largely to their unique ability to self-assemble into soft nanostructures.\textsuperscript{[12]} Within this broad classification, linear ABA triblock copolymers and higher-order multiblock copolymers with at least one midblock provide the added, and often desirable, benefit of forming a contiguous network consisting predominantly of bridged midblocks that physically connect the copolymer nanostructure.\textsuperscript{[13]} In this study, we focus on a block ionomer derived from a network-forming copolymer in the presence of a midblock-selective, low-volatility polar solvent. Consider, for illustrative purposes, an ABA triblock copolymer preferentially solvated with a B-selective solvent under equilibrium conditions. In the limit of high solvent concentrations, copolymer molecules self-organize into spherical micelles, each with an A core and a B corona.\textsuperscript{[14]} While the long-range order of these micelles may become compromised, the network connecting the micelles remains intact unless the copolymer concentration is reduced below the critical gel concentration. Within a midblock-solvated network, micelles composed of glassy or semi-crystalline endblocks serve as network-stabilizing cross-link sites, thereby making such elastomeric gels suitable for a wide range of applications, including dielectric elastomers,\textsuperscript{[15]} pressure-sensitive adhesives\textsuperscript{[16]} and microfluidic substrates.\textsuperscript{[17]} Recently, we have provided\textsuperscript{[18]} evidence to show that this design can be used in conjunction with a midblock-sulfonated pentablock ionomer (PBI) to generate highly responsive and stable
IPMCs. In this work, we more closely explore the performance of these IPMCs under different preparation conditions and in different solvents.

The PBI employed here is a poly[p-t-butyl styrene-b-(ethylene-alt-propylene)-b-(styrene-co-styrenesulfonate)-b-(ethylene-alt-propylene)-b-p-t-butyl styrene] ionomer, the chemical structure of which is displayed in Fig. 6.1a. While previous studies\textsuperscript{[19]} have shown that endblock-sulfonated styrenic triblock copolymers can yield IPMCs, it must be recognized that the endblocks in the current system are incompatible with polar solvents and therefore form the glassy microdomains required for network stabilization, as schematically depicted in Fig. 6.1b. In the presence of a polar solvent, the sulfonated midblock of each molecule becomes highly swollen in a solvent-rich matrix and, for the most part, adopts either a bridged or looped conformation. Under equilibrium conditions (achieved, for instance, by mixing the copolymer and solvent together, followed by increasing the temperature to form a solution and then decreasing the temperature to promote copolymer self-assembly), endblock-rich micelles surrounded by a rubbery shell uniformly disperse throughout the solvent-rich matrix. The present study, however, utilizes a nonequilibrium process strategy (detailed in the Experimental Section) to generate mesogels,\textsuperscript{[20]} which retain morphological features of the solvent-free copolymer. The existence of a bridged-midblock network connecting, and stabilized by, glassy endblock-rich microdomains can be confirmed by dynamic rheology. Frequency (\(\omega\)) spectra of the storage (\(G'\)) and loss (\(G''\)) moduli acquired at ambient temperature in the linear viscoelastic regime are shown in Fig. 6.1c for the PBI selectively swollen with two hydrophilic solvents used here: glycerol (GLY) and ethylene glycol (EG) at their maximum solvent uptake levels (\(~450\) and \(~500\) wt\% GLY and EG, respectively).
respectively). Two signature features evident in this figure are consistent with a physically cross-linked network:[21] (i) $G' > G''$ over the entire $\omega$ spectrum explored (confirming the load-bearing capability of the network), and (ii) $G'$ is weakly (if at all) dependent on $\omega$ (indicating a long relaxation time that is beyond experimental timescales) and nearly parallel to $G''$.

In general, IPMCs are fabricated from a polyelectrolyte membrane whose surfaces are coated with metals such as Pt, Au or Ag.[7,22,23] The IPMCs generated here begin with water-swollen PBI films that are subjected to Pt chemical deposition to metalize the inner surface, followed by surface electroding with Ag. Since the electrodes must establish a large contact area with the polyelectrolyte to achieve satisfactory capacitance, the electrode morphology constitutes a critical design consideration. Good interfacial adhesion between the electrode and polyelectrolyte is required for an efficient electric double layer, which, in turn, governs the storage capacity (and actuation strain) of IPMCs.[24] During conventional IPMC fabrication, a polyelectrolyte membrane is subjected to surface roughening and mechanical prestrain to improve the adhesion and distribution of the electrode metal along the polymer/metal interface. Since PBI swells extensively in deionized water at elevated temperatures and then collapses in the tetraamine platinum(II) chloride hydrate solution used for Pt electroding (due to salting-out), no such surface pretreatment is required in the present study. This feature, coupled with our ability to vary the number of Pt coatings applied, permits precise control over the distribution of Pt to desired depths within the membrane, which dictates the effective interfacial area and, in so doing, governs the actuation performance, as discussed later. On the basis of the findings reported by Lu et al.,[25] we first
apply one or more Pt inner-surface electrode layers, followed by an Ag surface electrode layer,\textsuperscript{[23]} to improve actuation performance. The distribution of Pt in the IPMC after each Pt deposition cycle has been probed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), and results obtained after 3 consecutive cycles are presented in Figs. 6.2a-c. The cross-sectional SEM image displayed in Fig. 6.2a reveals that the PBI membrane is sharply delineated from the top and bottom electrode layers composed of Pt and Ag. The Pt layer is not readily observed after a single coating, but it becomes increasingly evident upon deposition cycling.

Corresponding elemental x-ray maps acquired by EDS are shown in Figs. 6.2b-c for 3 Pt deposition cycles and confirm the spatial distribution of Pt (Fig. 6.2b) and Ag (Fig. 6.2c). It is important to recognize that, although Ag is restricted to the outer surface, Pt migrates into the membrane upon deposition cycling. This aspect of the IPMC electrodes is more clearly seen in the EDS line scans provided for 1, 2 and 3 cycles in Fig. 6.2d. As the number of deposition cycles is increased, a Pt layer measuring up to ~90 \( \mu \text{m} \) deep develops, and the concentration of Pt within the membrane correspondingly increases. In contrast, electrode metals are found\textsuperscript{[26]} to penetrate to only 10-20 \( \mu \text{m} \) in Nafion®. The Ag surface electrodes measuring 30-40 \( \mu \text{m} \) thick reduce the surface resistance to 2 \( \Omega \), which ensures that the potential along the entire length of the actuator is relatively uniform during testing. Recall that the electrodes are sequentially applied to both surfaces of water-swollen IPMCs. If desired, the water can be replaced by other polar solvents, such as GLY and EG, that are miscible in water. Regardless of the nature of the solvent, the free acid form of the ionomer is exchanged with Li ions, which promote substantially increased solvation. Application of an
electric potential across the thickness of the IPMC results in bending actuation, as illustrated by the schematic diagram presented in Fig. 6.1b and confirmed by the real-time sequence of superimposed images (discussed later) shown in Figs. 6.3a and 6.3b. While several mechanisms have been proposed\cite{27} to explain such actuation, one of the most widely accepted models is based on the microelectromechanical (MEM) model proposed by Asaka and Oguro.\cite{28} Recent neutron imaging and fluorescence microscopy studies performed by Park et al.\cite{8} and Park et al.,\cite{7} respectively, provide direct experimental evidence of this mechanism in IPMCs composed of Nafion®.

The MEM mechanism requires a potential-driven spatial redistribution of counterions and solvent molecules within the ionomer membrane of the IPMC. In the cantilever test configuration, the electric potential causes solvated cations to migrate towards the cathode, thereby increasing the electro-osmotic pressure of the ionic clusters along that side of the specimen. As solvent enters the clusters, the internal strain in the polymer matrix swells the interfacial boundary layer separating the cathode and membrane, and a solvent/counterion gradient forms across the membrane. Due to depletion of solvent molecules and counterions at the anode, the boundary layer separating the anode and membrane contracts. Concurrent swelling and contraction along opposite boundary layers and about the neutral plane results in the IPMC bending towards the anode. The rate at which, as well as the extent of which, bending occurs depends sensitively on several material characteristics, including the morphology and composition of the membrane, the quality of the solvent, and the nature of the neutralizing cation. The two most commonly employed polyelectrolytes used in IPMC actuators are Nafion® (and chemically-related analogs) and endblock-sulfonated triblock
copolymers. Unlike Nafion® [29], the PBI introduced here affords (i) facile processing in solvents without sacrificing useful mechanical or conductive properties, (ii) considerably higher solvent absorption levels, (iii) tunable morphologies in terms of nanostructural dimensions and anisotropy, and (iv) precise control over electrode morphology. Solvent processing can be used to tailor membrane dimensions, whereas solvent uptake determines the ionic conductivity of IPMCs and their actuation efficacy. Since most prior studies of IPMCs rely exclusively on the use of Nafion®, control over membrane morphology provides a largely unexplored route by which to alter ion and solvent transport and, thus, the rate and extent of actuation. While endblock-sulfonated triblock copolymers have, in fact, been used [19] to a limited extent as IPMC membranes, introduction of a polar solvent plasticizes the glassy endblocks and compromises the mechanical properties of such IPMCs at the solvent concentrations needed for satisfactory conductivity. This trade-off is not encountered in the current PBI membrane design.

The electromechanical performance of IPMC actuators is quantified by measuring cantilever deflection relative to zero load. In this work, measurements have been conducted at electric potentials ranging from 0.5 to 9 V, depending on the solvent employed. Although most of the results presented here correspond to organic (GLY and EG) solvents, water is used initially to permit comparison with other IPMCs, as shown in Fig. 6.3c. Bending deflections generated here with a dc potential of 1 V are marginally greater than those achieved with Nafion® actuated with an ac potential of 1 V at 0.5 Hz. Note, however, that the PBI investigated here yields actuation levels that are more than 3x greater than an IPMC derived from an endblock-sulfonated triblock copolymer subjected to a dc potential of 1 V,
and more than 6x greater than an IPMC fabricated from Nafion® (exchanged with Na ions) under a dc potential of 2 V. While the PBI membrane requires more time (~30 s) to achieve full actuation and the Nafion®-based IPMC actuates to its maximum in ~5 s, the latter also shows considerably greater evidence of back relaxation, in which the IPMC subjected to continued electrical bias changes its actuation direction (i.e., towards the original, zero-load position) after reaching a maximum forward deflection. Back relaxation has been previously reported to depend on the nature of the ionic moiety present on the polyelectrolyte backbone and molecular-level relaxation processes associated with the polymer chains comprising the membrane. Actuation tests using water as the conductive solvent are limited by the relatively low normal boiling point and electrolysis potential of water. To avoid these limitations and reduce the extensive likelihood of oxidizing the electrode metals, we have elected to use GLY and EG in the remainder of this study. Their normal boiling points are 290 and 197°C, respectively, whereas their corresponding electrolysis potentials are ~10 V for GLY and ~4 V for EG. One drawback to using organic liquids instead of water is that their viscosities are significantly higher (934 cP for GLY and 16 cP for EG, relative to 1 cP for water, at 25°C), which is expected to result in markedly slower actuation rates.

A sequence of digital images acquired during actuation of a GLY-containing IPMC fabricated from the PBI (with 3 Pt electrode coatings) and exposed to an electric potential of 7 V is displayed in Fig. 6.3a. This sequence demonstrates that the active length (L) of the IPMC (not gripped at the clamps) undergoes significant bending deflection upon actuation, the extent of which is measured in terms of the dimensionless parameter $\kappa L$, where $\kappa$ is the
curvature (equal to the reciprocal of the radius of curvature) of the IPMC cantilever strip. Values of κL extracted from digital images such as those in Fig. 6.3a confirm that bending proceeds to a plateau level and that the magnitude of bending increases with (i) the number of Pt coatings applied and (ii) the applied potential up to 7 V. At higher potentials (9 V, not shown here), the actuation level decreases due presumably to observed loss of solvent through the nanoporous Ag electrode during actuation. Included for comparison in this figure are actuation kinetics of IPMCs produced with Nafion® exchanged with different ionic species and actuated in GLY at 2 V. As in Fig. 6.3c, Nafion®-based IPMCs actuate more quickly than those containing the PBI membrane, but the Nafion® systems also exhibit considerable back relaxation while the potential remains applied. Back relaxation, which hinders control of actuator motion and peak force, is not evident in the PBI-containing IPMCs, but relaxation back to zero deflection ensues upon removal of the potential. It is of further interest that the IPMCs fabricated from Nafion® with K ions bend, for the most part, towards the cathode following a small initial deflection toward the anode. Similar behavior, however with no initial bending towards the anode, is observed with the PBI membrane (and Li ions) swollen with EG, as evidenced by the images shown in Fig. 6.3b and the extracted data presented in Fig. 6.3e.

The sequence of images provided in Fig. 6.3b verifies that the IPMC undergoes substantial bending toward the cathode upon electrical actuation. As far as we are aware, this is the first time that the direction of bending actuation is solvent-regulated, holding all other parameters constant. Although the precise reason for this unexpected behavior is not known at this time, we hypothesize that it is a consequence of the chemical interaction between EG
molecules and the functional groups on the PBI chains or the mobile Li ions, and is not due to viscosity differences. As with GLY in Fig. 6.3d, the extent of actuation increases to a plateau level as the electrical potential is increased to 1.0-1.5 V, beyond which a reduction in bending is observed most likely for the same reasons offered to explain the maximum voltage encountered with GLY. When the voltage is removed, no back relaxation occurs, further confirming that solvent quality plays a critical role in the fabrication of PBI-containing IPMCs with targeted actuation properties. To compare the transport properties of the data presented in Figs. 6.3d and 6.3e, we apply the MEM framework\textsuperscript{[28]} to account for bending as a function of time (t), but recognize that other models are likewise available for this purpose. According to this theory (originally developed for water-swollen IPMCs), the curvature of an initially flat membrane can be conveniently written as

$$\kappa = \frac{\Psi'}{D_m} \left[ 1 - \exp\left( -\pi^2 D_m t/W^2 \right) \right]$$ \hspace{1cm} (1)

where $\Psi'$ for a given specimen under actuation is a constant that depends on several parameters, including the thickness (W), equilibrium solvation and modulus of the membrane, as well as the diffusivity ($D_m$), density and transfer coefficient of the solvent, and the applied current density. Regression of Eq. 1 to the data yields the solid lines included in Figs. 6.3d and 6.3e and the values of $D_m$ provided as a function of applied voltage in Fig. 6.3f. For comparison, the value of $D_m$ for water in a Nafion®-based IPMC at 25°C is \~4.5 \times 10^{-6} \text{ cm}^2/\text{s},\textsuperscript{[28]} whereas those for GLY and EG in the PBI tend to be lower, ranging from about 3 \times 10^{-6} \text{ cm}^2/\text{s} for EG to 1 \times 10^{-7} \text{ cm}^2/\text{s} for GLY.
Maximum values of $k_L$ measured from this study are compared with those from previous efforts in Fig. 6.4 and immediately reveal that IPMCs containing the PBI membrane swollen with GLY are capable of substantially larger actuation levels at higher voltages. This figure also provides insight into the dependence of actuation on the number of Pt deposition cycles. We hasten to point out that if the number of Pt cycles is increased to 4, the actuation properties deteriorate as a percolated network of Pt develops and permits uninterrupted current flow. In addition, the results displayed in this figure confirm that the direction of actuation can be controlled by judicious selection of the solvent employed. Thus, incorporation of the PBI membrane into an IPMC permits tunable bending actuation and direction at high solvent concentrations without sacrificing the mechanical integrity of the IPMC. The novel multicomponent design afforded by the PBI membrane can provide unprecedented access to next-generation IPMCs with controlled morphology and, hence, ion/solvent transport properties and (electro)mechanical properties.

Experimental

The PBI used here was generously supplied by Kraton Polymers (Houston, TX). The sizes of the blocks (cf. Fig. 6.1a) in the non-sulfonated parent copolymer were approximately 15 (tbS), 10 (EP) and 28 (S) kDa. As reported by the manufacturer, the midblock was about 57 mol% sulfonated, and the ion exchange capacity (IEC) of the PBI was 2.0 meq/g polymer. Reagent-grade tetrahydrofuran (THF), GLY, EG, and lithium chloride were purchased from Fisher Scientific and used as-received. Tetraamine platinum(II) chloride hydrate was obtained from Aldrich. The PBI was dissolved in THF to form 2 wt% solutions, which were
subsequently cast into Teflon molds to form films that were annealed at 60°C for 24 h under vacuum. These films, measuring ~400 μm thick, were swollen with GLY or EG at 60°C overnight, and the resulting materials were analyzed on a Rheometrics Mechanical Spectrometer (RMS 800) equipped with 8 mm parallel plates separated by a 1-2 mm gap. The linear viscoelastic (LVE) limits at ambient temperature were determined by performing dynamic strain sweeps from 0.5 to 10% strain amplitude at a frequency of 1 rad/s. Frequency spectra were acquired at a strain amplitude of 1% in the LVE region. Fabrication of IPMCs required the formation of electrodes on the top and bottom surfaces of solvent-cast films. This involved two steps: initial compositing and surface electroding. In the first step, the top and bottom Pt electrodes were formed on a water-swollen PBI film by electroless deposition of Pt, as described elsewhere. This procedure was repeated up to 4 times. Surface electroding resulted in the formation of Ag electrodes on top of the Pt electrodes by the silver mirror reaction. As the reaction proceeded, discrete Ag particles deposited on the film surfaces and formed a contiguous layer. The dried membrane/electrode assembly thus obtained was examined by scanning electron microscopy (SEM) conducted in a Hitachi S3200 variable-pressure instrument operated at 20 kV in the presence of He at a pressure of 100 Pa. Samples were frozen in liquid nitrogen and cross-fractured to differentiate the layered morphology without the use of a conductive coating. An Oxford Isis EDS system was used to measure the spatial distribution of the electrode metals. For electromechanical characterization, fabricated IPMC films with electrodes were swollen in water, followed by immersion in a 0.5 M lithium chloride solution for 24 h at 60°C to promote Li ion exchange. Each film was subsequently submersed in a predetermined organic solvent at 60°C for 12 h
to produce a mesogel (which retains morphological characteristics of the PBI prior to introduction of solvent) and then cut into pieces measuring 3 mm x 25 mm. One end of the cut strip was clamped, and a free (active) length (L) measuring 1.9 to 2.0 cm long was continuously monitored as a predetermined electric potential was applied through the clamps. Recorded digital footage was analyzed by the Matrox Inspector software to determine the level of bending actuation from the radius of curvature along L.

Acknowledgments

This study was funded by the National Science Foundation, and K. E. R. gratefully acknowledges support from a National Science Foundation Graduate Fellowship. We thank Professor S. A. Khan for use of his laboratory facilities.
Figure 6.1 (a) Chemical structure of the PBI block ionomer possessing $p$-$t$-butyl styrene [tbS] endblocks separated from the styrene-$co$-styrenesulfonate [S(sS)] midblock by flexible ethylene-$alt$-propylene [EP] linkages. (b) Schematic illustration of the idealized microphase-separated morphology of a midblock-swollen PBI film — the copolymer shading matches that in (a) — and the resulting actuation mechanism of IPMCs prepared therefrom. (c) Frequency spectra of the PBI selectively swollen with GLY (open symbols) and EG (filled symbols). The dynamic storage ($G'$, circles) and loss ($G''$, triangles) moduli are labeled.
Figure 6.2 (a) SEM cross-sectional image and corresponding elemental x-ray maps of (b) Pt and (c) Ag after 3 Pt deposition cycles. Line scans collected from cross-sectional x-ray maps for Pt (light line) and Ag (dark line) are included in (d) for IPMCs subjected to 1, 2 and 3 Pt cycles.
Figure 6.3 Digital image sequences of PBI-based IPMCs acquired during electroactuation with (a) GLY and (b) EG at 7 and 1 V, respectively. (c) Actuation-induced bending deflection of Li-exchanged, hydrated PBI (●) at 1 V. For comparison, deflection results
reported for hydrated IPMCs composed of an endblock-sulfonated triblock copolymer (☐) at 1 V\textsuperscript{[19]} and Li-exchanged Nafion\textsuperscript{®} (dashed line) at 1 V and 0.5 Hz\textsuperscript{[19]} and Na-exchanged Nafion\textsuperscript{®} (△) at 2 V\textsuperscript{[30]} are included. (d) Bending actuation as a function of time for IPMCs consisting of GLY-solvated PBI (labeled with the cation and applied voltage) and Nafion\textsuperscript{®} (labeled with the cation in parentheses) at 2 V.\textsuperscript{[26]} (e) Bending actuation as a function of time for IPMCs consisting of EG-solvated PBI (labeled with the cation and applied voltage), as well as Nafion\textsuperscript{®} (△,○) and Flemion\textsuperscript{®} (□) (each labeled with the cation and applied voltage in parentheses).\textsuperscript{[26]} In both (d) and (e), the effect of Pt coating on bending actuation is shown for PBI-based IPMCs (☐, labeled with the number of Pt cycles) at 7 and 1 V, respectively. The dashed lines in (d) and (e) serve to connect literature data, whereas the solid lines correspond to regressions of Eq. 1 to data collected here. The bending direction of the IPMC is identified by the background shading: anode (white) or cathode (gray). (f) Values of D\textsubscript{m} extracted from the regression analyses in (d) and (e) and presented as a function of electric potential for PBI-based IPMCs solvated with GLY (circles) and EG (triangles) and subjected to 2 (filled) and 3 (open) Pt deposition cycles. The solid and dashed lines in (f) serve to connect the data.
Figure 6.4 Maximum bending actuation achieved for IPMCs fabricated from the PBI investigated in this work. Shown here are the IPMCs with GLY (filled symbols) and EG (open symbols), each labeled with the number of Pt deposition cycles. Error bars correspond to the standard error. The cross-hatched region identifies the range of actuation levels achieved for conventional IPMCs under similar test conditions. Background shading is the same as in Fig. 6.3, and the solid lines serve to connect the data.
References


7 Preparation and Characterization of Midblock Sulfonated Poly[styrene-\textit{b}-
butadiene-\textit{b}-styrene] Triblock Ionomer

7.1 Introduction

Most of the work done on ionic block copolymers either involves sulfonated diblocks
or endblock-sulfonated ABA type triblock copolymers. Amongst these, sulfonated ABA
triblocks (ionomers) are particularly intriguing in that they are capable of forming three-
dimensional networks on undergoing microphase separation of the blocks. If in ABA, A is
glassy and a minority component and B is rubbery at ambient conditions, the network gets its
stability from the glassy A domains that are connected to each other by bridges and entangled
loops\textsuperscript{1,2} of B blocks. The network provides excellent elastomeric properties to the ionomers.\textsuperscript{1}
The ionomers additionally offer improved thermal and mechanical properties over the parent
copolymer.\textsuperscript{3} Potentially, a non-polar midblock selective solvent such as mineral oil can be
added into these ionomers to form gels, similar to those formed by unsulfonated ABA
copolymers, that can be used in adhesives, as shock absorbents and as highly tunable
dielectric electroactive polymers capable of operating at higher working temperatures.\textsuperscript{4}
Oppositely, a polar solvent such as water can be added to swell these materials to be used as
polyelectrolyte membranes (PEMs)\textsuperscript{5} or as ionic electroactive polymers, for example, as
ionic-polymer metal composites (IPMCs).\textsuperscript{6} Each application demands some unique
properties of these ionomers. For instance, in IPMCs, water (or a polar solvent) uptake and
ion transport are critical parameters as they actuate to undergo mechanical deformation under
the applied electric potential by a mechanism that involves ion and solvent transport. High uptakes are desired to achieve higher mechanical deformations. Ion and solvent transport properties are, in turn, affected by microstructure of the ionomer.

The swelling behavior or solvent uptake is critical to several applications including PEMs and IPMCs. In applications where higher uptakes are desired, it is expected that the material retains its mechanical integrity on swelling. This is difficult to achieve in endblock sulfonated ABA ionomers of the type mentioned above. The solvent uptake that proportionately increases with the level of ionic content in the ionomer, compromises the mechanical properties of the ionomers by plasticizing A domains in endblock sulfonated ABA ionomers. Approaches, within block ionomers, to overcome this behavior are widely sought after. One approach is to crosslink the endblocks or the midblocks chemically after microphase separation, while the other is to introduce the ionic groups on to the B blocks. Out of these, the second approach is more appealing as it can potentially make thermal processing a possibility for these ionomers. Other features, such as tuning morphology, that affects transport properties, would be available irrespective of the approach used due to mere virtue of blocky nature of the block copolymers and also due to the possibility of tuning each block independently without affecting the other blocks. Additionally, morphology and other properties can be tuned by varying parameters such as molecular weight of the parent copolymer, block composition, ionic levels etc.

Midblock-sulfonated triblock ionomers have been reported several times in the past with the earliest report dating back to the work of Valint and Bock. They investigated poly[tert butylstyrene-\(b\)-styrene-\(b\)-tert butyl styrene] for its solution properties on sulfonation
of the midblock. Their synthetic approach was later used by Yang and Mays et al.\textsuperscript{9} to synthesize different architectures of the copolymer with the same blocks and then sulfonating their polystyrene block. Recently, Saito et al.\textsuperscript{10,11} have reported a midblock-sulfonated poly[hexyl methacrylate-\textit{b}-styrene-\textit{b}-hexyl methacrylate] and poly[perfluorooctyl methacrylate-\textit{b}-styrene-\textit{b}-perfluorooctyl methacrylate], where polystyrene was sulfonate by using acetyl sulfate. The focus of their studies was to obtain conductive membranes at reduced solvent uptakes for PEM applications. Szczubialka et al.\textsuperscript{12,13} in late 90’s, reported a midblock sulfonation of poly[styrene-\textit{b}-butadiene-\textit{b}-styrene] by a 1,4 sulfur trioxide:1, 4 dioxane complex as a sulfonating agent. Their work focused on the association behavior of the hydrophobic endblocks in aqueous solutions. Their method was subsequently used to sulfonate SBS in one of the co-author’s laboratory for making reactive stabilizers for emulsion polymerization.\textsuperscript{14} Recently, a chlorosufonic acid: 1, 4-dioxane complex has been reported to sulfonate butadiene blocks of SBS.\textsuperscript{15}

Amongst the several routes reported above, the one used by Szczubialka et al. is especially important as it can be practiced on commercially available SBS copolymers. In all the reports on midblock sulfonation of SBS, the objective was to prepare water soluble amphiphilic block ionomers, which was achieved by keeping S block molecular weight relatively lower than the sulfonated B block. In this work, the sulfur trioxide:dioxane chemistry was used to obtain sulfonated SBS from SBS having long S endblocks so that the formed ionomers were insoluble in water, but were highly swelleable in polar solvents and form a mechanically stable film, in the dry (and also later in solvated) state. Such a film can potentially be used in fabricating IPMCs\textsuperscript{16} or in healthcare products due to its excellent
solvent absorptivity. Although SBS has been sulfonated by this route by over a decade, though by a limited number of research groups, the properties of the thus formed ionomers in the dry (non-solvated) state have not been investigated. Literature indicates that the thermal properties of the ionic polymers can be very different than the non-ionic parent polymers. Investigating thermal properties of the prepared ionomers formed the first objective of this work, which was undertaken after the detailed characterization of the sulfonation reactions. Also, based on the reports that the microstructure of the copolymers can get affected by the introduced ionic groups in the polymer backbone and their concentration\textsuperscript{5,17}, an understanding of the microstructure was achieved using X-ray scattering experiments. Lastly, an insight into the type of micelles formed in the ionomer films is provided based on solvent uptake experiments and observed mechanical handleability in the swollen state.

7.2 Experimental procedures

7.2.1 Materials

A symmetric triblock copolymer of poly[styrene-\textit{b}-butadiene-\textit{b}-styrene] (SBS) of molecular weight 140000 g. mol\textsuperscript{-1} having 30 wt% S (as per the manufacturer) was obtained from Sigma Aldrich, Germany. The reagent 1, 4-dioxane extra pure was obtained from Riedel-de Haen, and extra pure fuming sulfuric acid with 65% SO\textsubscript{3} was from Merck, Germany. Hereafter, the polystyrene (either in SBS or homopolymeric) and polybutadiene (in SBS) are referred to as S and B respectively.
7.2.2 Sulfonation

The sulfonation of the copolymer was performed by a previously reported procedure used to prepare water-soluble midblock-sulfonated amphiphilic SBS copolymer having short polystyrene endblocks. The sulfonating agent was prepared by adding the corresponding amount of fuming sulfuric acid (65% free oleum) dropwise into 1, 4- dioxane upon stirring. The ratio of 1, 4- dioxane to sulfuric acid of 10:1 was used. The mixture was stirred at room temperature for 2h. A 5 wt% copolymer solution in 1, 4- dioxane was prepared. Batch size was kept constant to 3g of copolymer. The solution was then added to a jacketed reactor that had attached to it a condenser for cooling the evaporated reagent during the heating step of the reaction. The jacket facilitated heating/cooling by circulation of hot/cold water. Based on the desired degree of sulfonation of the butadiene block (DOS), a predetermined amount of the sulfonating agent was added to the reactor by an addition funnel while the polymer solution was kept stirring at 25°C. The reaction mixture was stirred for 2 h during which double bonds undergo cycloaddition reaction to form β- sultone. After 2 h of stirring, extra-pure deionized water of the same amount with dioxane was added and temperature was raised to 80 °C and maintained for 30 min. Water served to cleave sultone rings and formed the final product. The reaction mixture was dialyzed with de-ionized water as its conductivity was monitored. A portion of the dialyzed product was freeze-dried (Christ LMC-2, Osterode, Germany) to obtain dry sulfonated copolymer (ionomer). The remaining product was stored in refrigerator in closed containers without drying along with the dried product. By varying the concentrations of the sulfonating agent DOS of the ionomers was varied and three levels of sulfonations were achieved. The DOS was measured from 1H NMR
(explained later) and by elemental analysis using varioEL, Analysensysteme GmbH (Hanau, Germany) analyzer. The non-dried product was cast into teflon beakers as solvent (mostly water with some residual 1, 4- dioxane) was allowed to evaporate. The films obtained were flexible and yellowish-brown in color. They were not annealed and used as formed. Neat SBS was dissolved in 1, 4- dioxane and cast to obtain a film as solvent evaporated. This film was annealed in vacuum for 8 h at 135 °C to remove any residual solvent trapped in glassy S domains. The neat copolymer was designated as SBS00, whereas the ionomers as SBSxx, where ‘xx’ is a number indicating the DOS of the ionomer as determined from $^1$H NMR.

7.2.3 Sulfonation characterization

7.2.3.1 $^1$H NMR measurements

The deuterated tetrahydrofuran (THF) and water (D$_2$O) were obtained from Cambridge Isotope Laboratories, Inc., Boston, MA. The SBS00 was dissolved at room temperature overnight in deuterated THF from a freshly broken ampule. The freeze dried ionomers, were dissolved in deuterated THF+D$_2$O mixture (3:1) by heating at 50°C overnight. The $^1$H NMR spectra of these solutions were recorded using a Varian Mercury 400 MHz spectrometer. At 400 MHz, 256 scans were taken and peaks were referenced to solvent peaks.
7.2.3.2 FTIR-ATR measurements

Presence of sulfonic acid group was confirmed from FTIR-ATR spectra. The tests were performed on the neat copolymer and ionomer films. The equipment used was Thermo Electron FT-IR with Nexus 470 bench and ATR device was an ORBIT Sampler with diamond crystal. All FTIR spectra were taken with 128 scans with a frequency resolution of 4 cm\(^{-1}\) between the frequency range 4000-400 cm\(^{-1}\). Peak at 700 cm\(^{-1}\) due to out-of-plane deformation of ring CH was used to normalize the spectra for variation in film thicknesses.

7.2.4 Thermal characterization

7.2.4.1 Thermogravimetric analysis (TGA)

TA-Instruments Thermal Gravimetric Analyzer Q500 was used to determine the thermal stability of SBS00 and the ionomers. The samples were heated from ambient temperature to 600 °C with a ramp rate of 5 °C/min under a N\(_2\) atmosphere.

7.2.4.2 Differential scanning calorimetry (DSC)

Thermal transitions in the neat copolymer and the ionomer were determined by TA Instruments Q2000 model differential scanning calorimeter connected to liquid nitrogen for sub-ambient cooling. The instrument was calibrated with cyclohexane (-87.06 °C: solid-solid phase transition and 6.64 °C: melt transition) and indium (156.60 °C: melt transition). About 5-12 mg of sample was contained in standard aluminum pans. A pin hole was made into the
pan lid to facilitate evaporation of absorbed moisture from the samples in the first heating
scan. Two heating and cooling scans were performed at 10 °C/min in the temperature range
of -125 to 200 °C. The glass transition temperatures \((T_g)\) for B and S blocks, were
determined from the second heating scan. The onset and end of \(T_g\) for S was noted and the
difference in temperature between these two points was denoted by \(\Delta T_g\).

7.2.5 Microstructure characterization

SAXS measurements were performed on a Molecular Metrology SAXS instrument
with a sealed-tube source. Cu Kα radiation with a wavelength of 0.154 nm was used. A three-
pinhole collimation system produced a spot size at the sample of 700 µm. The raw data were
calibrated for the peak position with the standard silver behenate, which has peak position at
scattering vector, \(q = 1.076 \text{ nm}^{-1}\). The sample-to-detector distance was found to be 1.4 m
using the above calibration. Each profile was recorded at room temperature over a period of 1
h. The background (similar conditions without any sample) was subtracted from the intensity
of the scattered beam. The profiles are represented as a function of magnitude of scattering
vector, \(q\), which is related to the scattering angle, \(\theta\). The samples were in the film form as
cast from solutions without any annealing and hence retained the moisture absorbed or water
trapped from the casting process, the approximate amounts for which were calculated from
the ‘oven-drying’ experiments described below.
7.2.6 Solvent uptake measurements

The SBS00 and ionomers in the film form were weighed and then soaked in closed vials at room temperature for 24 h, after which they were taken out and wiped gently to remove excess solvent and weighed. Solvent uptake \( (U) \) was calculated by the equation given below. The sulfonic acid groups in the Ionomers are hygroscopic due to which the formed films absorbed moisture from air. This absorbed moisture in the films was evaluated by ‘oven-drying’ experiments and taken into account prior to calculating the solvent uptakes. These measurements involved drying of weighed ionomer films in vacuum oven for 24 h with a drying agent at 40 °C. The films were weighed after this and the weight loss incurred was ascribed to the absorbed moisture.

\[
U = \frac{W_{\text{film weight}} - W_{\text{dry film weight}}}{W_{\text{dry film weight}}} \times 100
\]  

(1)

7.3 Results and Discussion

Sulfur trioxide \( (\text{SO}_3) \) is a Lewis acid or an electron acceptor and hence can form coordination compounds with Lewis bases or electron donors such as pyridine and dioxane. The later reacts with one or two moles of \( \text{SO}_3 \) forming a 1-to-1 (Scheme 1) adduct or 2-to-1 adduct. The ratio of the complex is crucial and directs the reaction to sulfonating the aromatic hydrocarbons or unsaturated alkenes. Sulfonation of olefins by \( \text{SO}_3 \): dioxane complex has been known for more than a century and has proven important for sulfonating long chain \( \alpha \)-olefins used in surfactant applications. Reaction of \( \text{SO}_3 \) with olefins is a concerted cycloaddition reaction and is rigorous, which is moderated by complexing it with
dioxane. The 2-to-1 adduct sulfonates benzene, an aromatic hydrocarbon, at room temperature in a day, whereas in the presence of excessive dioxane, it shows no reaction in 3 days, and even at higher temperatures. Thus, on tuning the complex ratio, it can be used to selectively sulfonate unsaturated aliphatic blocks in a hydrocarbon block copolymer having aromatic and unsaturated aliphatic blocks.

In this work, the SO$_3$:dioxane was used to selectively sulfonate B block in SBS copolymer. The sulfonating complex is very unstable and hence was prepared immediately before the reaction. The complex once formed and added to the SBS solution in dioxane, reacted at the double bonds forming β-sultones. Later, on addition of water and temperature increase to 80°C sultone rings were cleaved (Scheme 7.1) by water to form the final product, which was purified as explained in the experimental section. By varying the complex concentrations, the DOS was controlled and the products were characterized by $^1$H NMR and FTIR.

7.3.1 Characterization and analysis of sulfonation reactions

7.3.1.1 $^1$H NMR measurements and elemental analysis

A typical $^1$H NMR spectra for the untreated copolymer, SBS00, and the sulfonated ionomer with the highest level of sulfonation, SBS81, are shown in Figure 7.1 (a). The spectrum for SBS00 was taken in THF solution and that for the ionomer was taken in a 3:1 mixture of THF and water. The spectra are composed of an aromatic zone from the phenyl rings of PS coming between 6.1 to 7.4 ppm. Two sharp peaks are seen in both the spectra at
1.73 ad 3.58 ppm corresponding to the incomplete deuteration of the solvent THF. In the ionomer spectrum, a third sharp peak at about 4.45 ppm was noted which was assigned to the residual undeuterated D$_2$O and the absorbed moisture in the ionomer due to its hygroscopic nature. In the plot, two more bands are also indicated. The first one is between 0.9 and 2.9 ppm representing protons associated with saturated carbons in the polymer that includes signal from both the blocks. The peak at ~ 2.10 ppm in this band corresponds to protons of CH$_2$ in 1, 4 unsaturated and CH of CH$_2$-CH in 1, 2 unsaturation. This peak progressively decreased as the sulfonation extent increased in ionomers. The last band shown in the figure is for the unsaturation in the butadiene units appearing between 4.75 and 5.75 ppm. Two peaks are labeled in this band: (1) peak A between ~ 5.10 and ~ 5.65 ppm and (2) peak B between 4.7 and 5.10 ppm. Peak A appearing as a doublet, is for two protons from 1, 4 unsaturation and one from 1, 2unsaturation in polybutadiene, while peak B is due to two protons of 1, 2 unsaturation.

The expanded spectra for SBS00 and all ionomers between 4.5-7.5 ppm are shown in Figure 7.1 (b). There are several observations that can be made from this figure. First, consider the peaks between 6.1-7.4 ppm. As the neat copolymer, only two peaks— (a) at ~ 7.0 ppm due to meta and para protons and (b) at ~ 6.5 ppm due to ortho proton on the aromatic rings— were seen in this region for the ionomers. The absence of a third peak corresponding to the meta protons in para-sulfonated polystyrene at about $\delta= 7.35$ ppm even at the highest sulfonation level (cf. Figure 7.1(a)) indicates that S was not sulfonated. The reaction with the same conditions as used for the highest sulfonation level acheived was performed on a homopolymeric polystyrene and the product was analyzed with $^1$H NMR
(data not shown). The spectrum was indifferent to the one for parent homopolymer further confirming that the reagents under the given reaction conditions do not react with S. The intensities of the peaks A and B in Figure 7.1(b) were seen to diminish progressively as the extent of sulfonation of the ionomer increased. The degree of sulfonation (DOS) was calculated by using equation 2 shown below,

\[
DOS = 1 - \frac{I_d / I_s}{(I_d / I_s)_0} = 1 - \frac{I_d / I_s}{C}
\]

where, \(I_d\) is the sum of intensities of peaks A and B, \(I_s\) is the intensity of the aromatic peaks between 6.1-7.4 ppm and \((I_d / I_s)_0\) or constant C represent similar ratio of the peak intensities for the parent copolymer. The calculated sulfonation (%) as a function of moles of SO\(_3\)/moles of polybutadiene is shown in Figure 7.2 The numbers in Figure 7.1 correspond to the degrees of sulfonation of the ionomers in %. The progressive decrease in A’s and B’s intensities with increasing DOS confirmed that the sulfonation reaction occurred at the butadiene units. The DOS varied nearly linearly with the concentration of SO\(_3\) expressed as a mole ratio on the abscissa. The DOS was also calculated from elemental analysis and the values obtained were in close proximity to those obtained from NMR. The trend, as was seen by the NMR, was linear.

From Figure 7.1(b), one can also note that the peak due to 1, 4 unsaturation reduced in intensity faster than the one for 1, 2 unsaturation as the DOS increased. The percentage sulfonation at the respective unsaturation was calculated by using equation 1, where now \(I_d\) stood for the intensity of the appropriate peak representing the corresponding unsaturation. The \(I_d\) for peak A was corrected to represent 2 protons from 1, 4 unsaturation. The values for
DOS are plotted in Figure 7.2 and confirms that 1, 4 saturation is more reactive than the 1, 2 saturation for sulfonation. This has been found true for other reactions such as epoxidation of polybutadiene. It should be noted that the spectra for ionomer shifted to higher magnetic field against that for the neat copolymer. This was likely due to solvent effects as D$_2$O was used to dissolve the ionomers along with THF and not for the neat copolymer. When peak A’s intensity obtained from peak integrals, location and shape was compared amongst the ionomer spectra, it was seen to reduce in intensity (as confirmed from sulfonation values shown in Figure 7.2), narrow down in width and shift to lower fields as DOS increased. Peak A represents the cis as well as trans 1, 4 unsaturation. The chemical shift of the later is at a lower field (higher ppm) than of the former. The peak shifting to higher ppm with increasing DOS, thus, indicated that cis 1, 4 unsaturation was more reactive to sulfonation and were consumed faster. The presence of sulfonic acid groups in the formed ionomers was confirmed by FTIR.

7.3.1.2 IR absorptions

Figure 7.2 shows the normalized FTIR spectra for SBS00 and the ionomers prepared. In SBS00 several peaks characteristic to B and S can be assigned. The peaks at 1600 and 1489 cm$^{-1}$ are for aromatic ring modes of S. The out-of-plane deformations of CH in S ring appear at 700 cm$^{-1}$ and 745 cm$^{-1}$. The peaks at 1451 and 960 cm$^{-1}$ depict CH$_2$ scissoring vibration and =CH out-of-plane deformation of CH=CH (trans 1, 4) in B. The band due to cis 1,4 comes nearly at the same location as 960 cm$^{-1}$ and is difficult to distinguish
separately. The peak at 913 cm\(^{-1}\) is from the out-of-plane wagging of =CH from CH=CH\(_2\) (due to 1,2 addition during polymerization). The 1641 and 3003 cm\(^{-1}\) represent C=C and =C–H (from =CH) stretches of B. A doublet at 2920 and 2832 correspond to CH antisymmetric and symmetric stretching of CH\(_2\) in B repeat units.

After sulfonation, three new peaks appear at 1030, 1138 and 1340 cm\(^{-1}\) in the spectrum for ionomers indicating the successful sulfonation of the copolymer. The sulfonation reaction under the similar conditions as used for SBS81 was performed on a homopolymers of styrene and NMR was taken on the product. The spectra of the untreated and treated polymers were indifferent (data not shown), thus confirming that the reaction does not sulfonate the styrene units. With this noted, it is safe to infer that only the butadiene block was sulfonated. The 1030 cm\(^{-1}\) peak, then, can be assigned to S=O stretch and 1138 to SO\(_3\) symmetric stretching. The peak 1340 cm\(^{-1}\) was also from the sulfonate group. The intensities of these three peaks increased progressively as sulfonation level (as determined from NMR) increased in ionomers from SBS38 to SBS81. Correspondingly, there was a decrease in intensities of peaks at 960 cm\(^{-1}\) and 913 cm\(^{-1}\) that, as listed above, was assigned to =CH out-of-plane deformation in CH=CH (trans 1, 4 and cis 1, 2, respectively) of B. The broad peak beyond 3200 cm\(^{-1}\) is due to the –OH stretch of the sulfonated butadiene and the absorbed water. This peak also increased in intensity as the sulfonation level increased indicating more moisture uptake which was expected. No attempt was made to quantitatively evaluate the degree of sulfonation from IR data as it would require elimination of water during sample preparation and measurement, which is difficult due to the hygroscopic nature.
of the ionomers. Thermogravimetric analysis and oven-drying experiments, as explained below, provided an estimate for the absorbed moisture content in the ionomers.

7.3.2 Thermal characterization

7.3.2.1 Thermal stability of the ionomers

The weight loss in SBS00 and ionomers with temperature is shown in Figure 7.4. The SBS00 showed onset for decomposition around 350 °C. The significant weight losses for ionomers occurred in three stages as delineated from derivative plot of the weight. A representative curve (DTG81) for SBS81 is shown in the figure. The temperature ranges for the three stages were 30-200, 210-280 and 335-525 °C. The stages are similar to those reported by Smitha et al. In the 30-200 °C, till about 80 °C the loss was assigned to the surface moisture of the ionomer films, beyond which up to 200 °C, the loss was from the moisture that was associated with the ionic groups. The release of absorbed moisture occurred over an extended temperature range due to the strong ionic interaction of the sulfonic acid moieties with water molecules. The absorbed moisture as evaluated from the oven-drying process valued at 9, 18 and 27% SBS38, SBS62 and SBS81 respectively. These values were lower than those from TGA seen in Figure 7.4 The discrepancy stemmed from using a very low temperature of 40 °C during oven-drying process, which likely was not high enough to remove all the water molecules associated with ionic groups. As the DOS increased so did the weight loss in this stage which agreed well with the expected increase in moisture absorbance by SO₃H groups. The loss in 210-280 °C is due to the splitting of
sulfonic acid groups. As DOS increased the wt loss in this stage increased. The last stage between 335 and 525 °C is for the final decomposition of the polymer backbone. The ionomers showed slightly higher backbone decomposition onset temperature than the parent copolymer in-line with previous reports for other endblock sulfonated triblock copolymers. The left over char was obtained after the test for all ionomers and hence, complete weight loss, as seen for SBS00 was not observed. As the temperature increases, along with the cleaving of sulfonic acid groups from the backbone, the sulfone formation also occurs from dehydration reaction of sulfonic acid groups that crosslinks the butadiene units. The sulfones are known to have improved thermal stability. Thus, the char is likely the sulfone-crosslinked block copolymer.

7.3.2.2 Thermal transitions in the ionomers

Having established the thermal stability of the ionomers, the next step was to investigate the thermal transitions and nature and quality of the microphase separation in these ionomers. Figure 7.5 shows that there are two Tgs for the neat SBS—one for the butadiene blocks at -91 °C and the other, a broad one, around 86 °C. The Tg for butadiene domains (cf. Figure 7.5a) disappeared in the sulfonated ionomers at all sulfonation levels studied. On sulfonation, the ionic groups in the butadiene block presumably form ionic aggregates and serve as crosslinks between the midblocks, thus, reducing the free volume and restricting the chain mobility. In the case of sulfonated poly[styrene-\textit{b}-(ethylene-\textit{co}-butylene)-\textit{b}-styrene] (SSEBS), where the endblocks were sulfonated, the endblock domains
showed an increased $T_g$ due to the same effect as seen here. In the SSEBS the ionic aggregates existed in the glassy polystyrene domains and significantly hindered the microphase separation resulting into deformed morphologies. For SBS, the sulfonic acid moieties were added on to the rubbery B chains, which aggregated into groups due their incompatibility with the hydrophobic matrix. Consequently, the ionomers had a two level of phase separations: 1. due to the block microphase separation, noted from the appearance of S domain $T_g$ equal to that for a homopolymer styrene, that is a characteristic of a block copolymer and 2. the ionic phase separation due to aggregation of sulfonic acid groups.

It was of interest to determine if the ionic phase separation in B matrix would affect the microphase separation between the B units and S blocks. This was evaluated from the $T_g$ of S domain. The neat SBS showed lower $T_g$ for S (Figure 7.6(b)) than that would be expected for a polystyrene homopolymer of same molecular weight as the S block. Our observation agreed well with the findings of Grainger et al., who in their studies on S-B diblock copolymers found that for the $T_g$ of S domain to equal that of homopolymeric polystyrene, S molecular weight should range between $3.5 \times 10^5$ to $7.1 \times 10^5$ Da, below which there is a depression in $T_g$'s of S block in a copolymer. It should be recalled that the S block molecular weight in the SBS used here is about 18 kDa. The depression in S block $T_g$ was due to inclusion of B block chains in the S domains termed as mixing-in-domain effect. The observed $T_g$ was also broad assigned to domain-boundary effect explained as the mixing of S and B chains at the interface. In the sulfonated ionomers, the S domain $T_g$ increased to ~99 °C for the 38% sulfonated copolymer and slightly increased thereafter for the higher sulfonation contents. The close proximity of the $T_g$ after sulfonation indicates that
the mixing-in-domain effects were minimized. This could be explained based on the thermodynamic incompatibility of the two blocks. This incompatibility is given by Flory-Huggin’s interaction parameter, $\chi$, which values at 0.08 for S-B copolymer.\textsuperscript{36} On sulfonation of the B block, this value would increase consequent to the increased polar nature of the sulfonated B units relative to the non-polar S blocks, making the mixing of two blocks inside the S domains difficult and promoting the exclusion of sulfonated B chains from the S domains. As a result, a rise in the styrenic $T_g$ occurred, which was much closer to that for homopolymeric styrene. As sulfonation increased the $T_g$ broadened, especially, for higher sulfonation levels and became less distinct. The broadening was seen by the increase in $\Delta T_g$, measured as a temperature difference at the endpoints of the horizontal line passing through the respective $T_g$. This increase $\Delta T_g$ indicated the occurrence of microphase separation with diffused S domain interfaces causing domain-boundary effects. The additional evidence for diffused S domain interface in the ionomers was provided by SAXS results.

7.3.3 Microstructure determination

The scattering patterns for SBS00 and ionomers are shown in Fig 6. The peaks seen in the explored q range are assigned to the two phases formed from microphase separation of S and B blocks. The ionic clusters in sulfonated copolymers would be expected to appear at much higher q values (0.5-2.5 nm\textsuperscript{-1}), not explored here, due to their much smaller size scales.\textsuperscript{37} The sequence of ratios of peak locations (q) to the first—principal—peak ($q^*$) was used to assign the morphologies. The peak ratios for SBS00 were $q^* : \sqrt[3]{q^*}$, which indicates that
the microstructure consists of hexagonally packed cylinders of S embedded in the matrix of B. Considering the fraction of the S block in the copolymer to be 30 wt% (27 vol%), the morphology agrees well with the expectation. The three peaks seen for SBS38 were located at q*, 2q* and 3q*, whereas in SBS62 the only two peaks seen were located at q* and 2q*. The peak locations for these ionomers indicate that they consist of lamellae of S and sulfonated B blocks. The SBS81 showed one higher order peak. The peak locations for this ionomer did not match with any known conventional morphologies suggesting the possibility that the microphase separation was hindered due to possible interference caused by formation of ionic aggregates. It is likely that this ionomer still has lamellar morphology, though it might not be well ordered.\textsuperscript{38} Our observation is in-line with the several studies\textsuperscript{39,40} reporting that non-periodic morphologies exist at high ionic contents. Also, recall that the ionomers films were not annealed, thus, the possibility of having non-equilibrium microphase separated morphologies exist. The block ionomer morphologies at high ionic contents remain to be an extremely fascinating research topic as it remains unclear how the microstructure of a block ionomer is affected as a function of its ionic contents.

The $q^*$ broadening seen for ionomers as sulfonation increased indicated that the S domains decreased in size and became less homogeneous.\textsuperscript{3} This peak broadening could be explained, as was done for DSC results, by the effect arising from the formation of ionic aggregates in the butadiene matrix. As the ionic aggregates formed, they reduced the mobility of S and B blocks in the chains and competed against the block microphase separation affecting its kinetics. This resulted in incomplete segregation of the blocks that then formed domains with diffused interface boundaries and with broader distribution of
center to center distances between microdomains. The SAXS results are consistent to the
trends in behavior of S domain $T_g$s obtained from DSC experiments.

When the scattering patterns for the ionomers are compared, a progressive shift in the
$q^*$ to higher wavevectors can be noted. The peak position of $q^*$ is inversely related to the
interdomain spacing, thus, suggesting that the interdomain spacing reduced with increase in
$DOS$. This observation is contrary to the expectation that the increased molar volume of the
polybutadiene repeat unit after sulfonation (about 99 cm$^3$/mol calculated from Group
Contribution Theory$^{11,41,42}$) from 60.6 cm$^3$/mol in the unsulfonated form$^{43,44}$ would swell the
B block and increase the inter-domain spacing that would appear by a shift in $q^*$ peak to
lower values. However, the counter observations make us hypothesize that the presence of
ionic groups is a reason for this ambiguity. We believe that the ionic groups due to their
electrostatic interactions formed ionic aggregates, which is known to occur even at low ionic
contents.$^{45}$ The formation of ionic aggregates is supported by our finding that butadiene’s $T_g$
disappeared in DSC on sulfonation. These ionic aggregates then demonstrate strong inter-ion
interactions as ionic contents increased, thereby progressively reducing the B domain in size
and making it denser. As the B matrix became dense, the B blocks pulled the endblocks of
the chains, and hence the micelles containing them, closer thus moving the $q^*$ positions to
higher values. One would expect that the densification of B bocks would change the relative
volume fraction of the S blocks, which now would be higher than in SBS00. Consequently,
the mean curvature at the S and B microphase separated interface would change. If this
occurred, the cylinder forming S domains in SBS00 would likely transform into alternating
lamellae in SBSxx. Meeting this expectation, ionomers showed lamellar morphologies as
assigned from SAXS patterns in Figure 7.6. Our explanation for the transition of morphologies assumes that the block ionomers obey the classical block copolymer phase theories and diagram. We understand this assumption may not be completely correct in light of the literature published so far. Also, it needs to be pointed out that there is a possibility that the transitions in morphologies could also have been an effect of using different solvents for casting SBS00 and SBSxx. Although changing the microstructures by varying solvents has been widely studied by several investigators for uncharged block copolymers, this has rarely been explored for block ionomers.

At this point, it needs to be mentioned that variation in SAXS patterns and morphologies in any block ionomer system should be considered on system-to-system basis as every system behaves uniquely, as for example, a companion midblock sulfonated copolymer of poly(tert-butylstyrene-b-styrene-b-tert-butylstyrene) that we recently investigated indicated that the principal peaks in SAXS shifted to lower scattering vectors with increasing sulfonation levels and micelles transitioned from cylinders to spheres shapes. More details on this system will be provided elsewhere. While considering the different block ionomer systems, the effects from factors such as absorbed moisture due to the hygroscopic nature of the ionomers and block chemistries that can influence the microstructures need to be considered, which so far have not been well established.
7.3.4 Qualitative assessment of micelle-type in ionomer films from solvent uptake experiments

As alluded to earlier, Szczubialka et al. were the first to our knowledge to prepare midblock-sulfonated SBS ionomers using the reaction procedure used in this work. The SBS in their case had long B blocks and short S endblocks that formed less than 30 wt% of the parent copolymer before sulfonation. Their investigations focused on the association behavior of the prepared ionomers in aqueous solutions and they found that the micellization occurred in them that depended on the concentration of the polymer and the ratio of S and B block lengths. They further proposed a hypothetical model for the type of micelles in these solutions as being flower-like, which can be bridged or non-bridged or a mixture of both depending on the ratio of block sizes. Since the ionomers made in this work fall in the same genre of ionomers as made by them, with the exception that S blocks were significantly longer and comprised > 30 wt% of the copolymer, it is expected that micelles belonging to either one or more of these types would be formed during the dialysis process based on the typical aggregation behavior of amphiphilic block copolymers under similar condition reported in literature.\textsuperscript{12,46} It is possible that the formed micelles can template the solid-state morphology as the solvents were subsequently evaporated. Though the detailed characterization of micellization behavior and its correlation with the observed microstructure in solid-state ionomers (reported in this work), forms a topic for future investigations, to obtain a qualitative understanding of the type of micelles that eventually populated the formed films, solvent uptake tests were done and thereafter mechanical stability was observed while handling. The ionomer films were swollen in deionized water
and glycerol for 24 hours at room temperature followed by measurement of solvent uptakes. Based on the ionic content the films absorbed the solvents to varying extents. The uptake increased as the sulfonation level increased (cf. Figure 7.6). The films remained intact, but were significantly weakened and fell apart with agitation. This behavior hinted that presumably the micelles formed were mostly flower-like, with a few connected by inter-micellar bridges. The intact form of films after imbibing the solvent indicated the small fraction of bridged micelles, while the difficulty with mechanical handling in the swollen state indicated the existence of majority of micelles as non-bridged, but looped. The contribution from ionic phase to providing the mechanical integrity is highly unlikely due to extensive plasticization of ionic aggregates with the solvent. The microstructure of the ionomers depends on the processing conditions such as the solvent used. Knowing that the ionomers are no longer soluble in water after sulfonation, one can tune their mechanical properties by re-dissolving the ionomers in a suitable solvent that would promote bridge formation between the micelles while casting them into films. This is something of interest for future explorations. An interesting observation to make from Figure 7.6 is that the sulfonated ionomer with the highest level of sulfonation can absorb up to 29 and 16 times of water and glycerol, respectively, of its dry weight making these ionomers a potential material for use in several hygiene and healthcare applications. The absorptivity can be controlled by varying the DOS.
A water insoluble block ionomers of SBS were prepared by selectively sulfonating the B blocks such that on microphase separation only the ionic B blocks get solvated by polar solvent leaving the glassy endblocks unaffected that continue providing mechanical stability to the material. The \(^1\)H NMR and FTIR-ATR techniques confirmed the sulfonation of only the B blocks and the variation in achieved DOS. The thermal behavior of the ionomers was significantly different than the parent copolymer. The \(T_g\) for the B blocks disappeared on sulfonation indicating that strong ionic interactions existed between ionic groups that formed aggregated, thereby restricting the chain mobility and densifying the B matrix. The chain restrictions on B block affected the microphase separation between the S and B blocks resulting into formation of S domains with diffused interfaces due to domain-boundary effects, which was concluded from the broadening of the styrenic \(T_g\). A further evidence for this was provided from SAXS, where the principal peak broadened with increasing DOS confirming that the S domains became smaller and inhomogeneous. The peaks also shifted to higher wavevectors progressively showing that the inter-domain spacing decreased. This was hypothesized to occur due to densification of the B matrix from ionic aggregate formation that pulled the endblocks, and hence the micelles containing the endblocks, closer. There was long-order observed in the ionomers till 62% DOS, beyond which the order was reduced due to the influence of ionic aggregates on the mobility of chains.

The ionomers formed in this study were not as much mechanically robust to survive agitation and facilitate facile handling, but were insoluble in water. The understanding obtained for the sulfonation reactions performed here and the evaluated properties can be
applied in designing new midblock sulfonated SBS-based ionomers with improved properties. The properties such as mechanical stability in the swollen state can be tuned by varying the block lengths, copolymer compositions, DOS and ionomer processing conditions such as the solvent used for making ionomer films.  

7.5 Acknowledgment

The authors would like to thank Prof. Christopher B. Gorman, Department of Chemistry, North Carolina State University, NC, for providing access to his research facilities for this work.
Scheme 7.1 Reaction steps. Butadiene is shown as obtained from 1, 4 addition reaction. The units resulting from 1, 2 addition are also present, but chosen not to be shown to maintain clarity in the figure.
Figure 7.1 Shown in (a) typical $^1$H NMR spectra of neat SBS denoted as ‘00’ and sulfonated ionomer with highest level of sulfonation indicated as ‘81’. The solvent peaks are labeled. The aromatic band, the aliphatic band due to protons in unsaturated butadiene units and the
aliphatic polymer backbone zone are labeled. In (b) expanded spectra between 4.5 and 7.5 ppm. The ionomers are labeled with numbers corresponding to their degree of sulfonation. Neat SBS was tested in THF solution, while the ionomer in solvent mixture of THF and water mixed in 3:1 ratio. The spectra are shifted vertically for convenience.

Figure 7.2 Total sulfonation (○) (connected by linear fit), sulfonation at 1,4 butadiene units (▲) and sulfonation at 1,2 butadiene units (◆) and (2) elemental analysis (◇) (connected by a linear fit).
Figure 7.3 Spectral scans for SBS00 and all ionomers SBSxx (labeled with number indicating DOS). The lines correspond to the wavenumbers listed along with them and indicate the peaks that appear after sulfonation of SBS. The scans are shifted vertically for clarity.
Figure 7.4 Thermal behavior SBS00 and all ionomers SBSxx (labeled with numbers indicating DOS). The dotted line is a derivative of the weight loss with temperature for SBS81 labeled as DTG81. The three stages of weight loss are shown in shades.
Figure 7.5 Shown in (a) the T_g of butadiene block by a hyphen and (b) the T_g of polystyrene block by vertical line-marker intersecting the curve. The ΔT_g's are shown by horizontal lines passing through the respective T_g's. The curves are shifted vertically for clarity. All T_g's were measured from the second heating cycle. The neat copolymer and ionomers are labeled by the degree of sulfonation.
Figure 7.6 SAXS scans for SBS00, SBS38, SBS62 and SBS81 as labeled. The arrow heads indicate the location of peaks in each respective curve. The dotted lines show how the principal peak position shift to higher q values on sulfonation, first for SBS00 to SBS38 and then for SBS38 to higher DOS ionomers.
Figure 7.7 Solvent uptake at ambient conditions after 24 h of soaking: water (○) and glycerol (△). The error bars for water are smaller than the marker size.
7.6 References


8 Characterization of and Morphology Development in Block Ionomers of Poly[(p-
tert-butylstyrene)-b-styrene-b-(p-tert-butylstyrene)]

8.1 Introduction

Block copolymers (BCs) have remained at the forefront of materials research due to their versatility in applications ranging from hot-melt/pressure-sensitive adhesives and impact modifiers to compatibilizers and vibration-dampening/nanotemplating media. They are mostly comprised of the two or more homopolymeric macromolecules such as polystyrene, polyethylene, poly(ethylene oxide), poly(methyl methacrylate), etc. linked covalently into a variety of architectures. The studies dealing with their phase behavior and thermodynamics have remained of interest over the last few decades. Detailed phase diagrams are available\(^1\) that are believed to have universal applicability to all the block copolymers.\(^2\) The composition of the blocks needs to be a key consideration while finding an appropriate phase diagram for a copolymer system. Interesting addition to the family of conventional block copolymers are the copolymers having one or more blocks that possess ionic moieties covalently linked to their backbones. We refer these type of copolymers as block ionomers. The sulfonic acid groups make the ionic species in most cases and they are introduced onto a specific block before or after the copolymer polymerization process. The block ionomers are an interesting class of materials and form a topic of discussion in this article.
The block ionomers are of importance as they find applications in actuators, sensors, water treatment and purification, batteries, as polyelectrolyte membranes and as ion-exchange resins. They are unique for two reasons: (i) they offer the features of both, the block copolymers and polyelectrolytes, and (ii) facilitate the possibility of tuning material properties by selective changes to one (or more) specified block(s) without affecting the others. They are also different than the homopolymers, with either charged or uncharged backbones, in one aspect, which is extremely valuable. The blocks in the block ionomers undergo microphase separation into a variety of morphologies such as cubic morphologies of spheres and gyroid, hexagonally packed cylinders, and alternating lamellae. This observed variety in microstructures serves as another key factor that can be used to tune material properties. For instance, properties such as ion transport and conductivity have been reported to depend on the morphology. The morphological transitions in block ionomer in response to variation in factors such as ionic content, block chemistry etc. are more complex than those seen in uncharged copolymers, and have not been well understood so far. The properties of block ionomers are not just affected by the morphology, but also by the periodicity in the microstructure. The science behind this observation is also not well understood. Several researchers have attempted to extend and apply theories for uncharged block copolymers to block ionomers in order to explain the complexity in their phase behavior, but with limited success as most of these theories fail to incorporate the ionic and dipolar interactions that exist in block ionomers. Establishing the phase behavior of block ionomers, thus, remains to be an intriguing area for researchers.
On evaluating what has been done with regards to sulfonated linear block copolymers, the work published can be classified into two types: (i) sulfonated diblocks such as poly(butadiene-\textit{b}-styrene) \text{(S-BS)}\textsuperscript{8, 9}, poly[styrene-\textit{b}-(ethylene-\textit{co}-propylene)] \text{(S-SEP)}\textsuperscript{10}, poly[styrene-\textit{b}-(vinylidene difluoride-\textit{co}-hexafluopropylene)] \text{[S-S(VDFHFP)]}\textsuperscript{11} and poly(styrene-\textit{b}-methylbutylene)\textsuperscript{6} and (ii) endblock-sulfonated ABA type triblock copolymers such as poly[styrene-\textit{b}-(ethylene-\textit{co}-butylene)-\textit{b}-styrene] \text{(S-SEBS)}\textsuperscript{12, 13}, poly[styrene-\textit{b}-(isobutylene)-\textit{b}-styrene] \text{(S-SIBS)}\textsuperscript{14} and poly[styrene-\textit{b}-(ethylene-\textit{co}-propylene)-\textit{b}-styrene] \text{(S-SEPS)}\textsuperscript{3}. Amongst these, the second type—sulfonated ABA architectured block ionomers—are particularly intriguing in that they are capable of forming three-dimensional networks on undergoing microphase separation of the blocks. If in ABA, A is glassy and forms a dispersed component and B is rubbery at ambient conditions, the network gets its stability from the glassy A domains that are connected to each other by bridges and entangled loops of B blocks.\textsuperscript{15} The network also provides excellent elastomeric properties to the ionomers. The ionic groups present in A block improve the mechanical and thermal properties of the ionomer over the parent copolymer.\textsuperscript{13} Potentially, a non-polar midblock selective solvent such as mineral oil can be added into these ionomers to form gels, similar to those formed by unsulfonated ABA copolymers, or oppositely, a polar solvent such as water can be added to swell these materials. The first approach can be used in designing new thermoplastic gels for applications such as shock absorbents, while the second approach is utilized in fuel cells when the ionomers are used as polyelectrolyte membranes (PEMs) or in actuator when used as electroactive polymers, for example, as ionic-polymer metal composites (IPMCs).\textsuperscript{16} Properties such as ion transport and solvent uptakes are important
when these block ionomers are used in presence of polar solvents in applications, such as PEMs and IPMCs. Since the glassy endblock domains in the endblock-sulfonated ABA triblock ionomers are responsible for providing mechanical stability to the material, on introducing a polar solvent such as water, mechanical properties are compromised. If the solvent content is reduced, the transport properties get affected. Thus, a compromise has to be found between the ionic content (that decides the solvent uptake) and the mechanical properties. To overcome this problem, midblock-sulfonated ABA block ionomers have been investigated recently, with only a few reports published so far.\(^\text{17, 18}\) The ionomers of this architecture are known for over a few decades now, but were made to suit a different purpose of making water soluble polymers that formed micelles in aqueous solutions.\(^\text{19, 20}\) A sulfonated SBS, where the B block has ionic groups has been prepared via 1, 4- dioxane: SO\(_3\) chemistry and its solution properties have been investigated. Recently, we have reported elsewhere, the bulk properties of the SBS ionomers prepared by this procedure. Saito et al.\(^\text{18}\) and Moore et al.\(^\text{17}\) reported midblock-sulfonated poly[hexyl methacrylate-b-styrene-b-hexyl methacrylate] (MSM) and poly[perfluorooctyl methacrylate-b-styrene-b-perfluoroctyl methacrylate] (OSO) block ionomers prepared by ATRP polymerization followed by sulfonation using a procedure similar to Makowski’s.\(^\text{21}\) The objective of their work was to make mechanically stable sulfonated block ionomers. The MSM ionomers had a low \(T_g\) of -6 to 0 °C, which would restrict their applicability only to low temperature applications. The OSO ionomers did not show well-defined morphologies and periodicity that could be a cause of concern during their application. One more example of the block ionomers of this type, referenced above, exists and was of particular interest to us due to the well-established
protocol for synthesizing its parent copolymer, which was used as a base material for sulfonation. These ionomers were based on poly(p-tert-butylstyrene-\textit{b}-styrene-\textit{b}-p-tert-butylstyrene) [TST] copolymers comprised of relatively short T blocks in the chains and were soluble in water. They were used mainly for studying their aqueous solution behavior.$^{19,20}$ In the current work, a TST copolymer with relatively longer T blocks than used in the previous studies was used to synthesize water-insoluble midblock-sulfonated ionomers that can microphase separate into networked microstructure. The structure gets its mechanical support from the glassy endblock domains that do not swell when a polar midblock-selective solvent is introduced.

In the past, Zhou et al. have sulfonated TS diblock copolymers by using Makowski’s procedure,$^{22}$ while Yang et al.$^{19,23}$ used a triethylphosphate:SO$_3$ complex to sulfonate the di- and triblock TS copolymers. In Yang et al.’s approach, concerns over the possibility of sulfonating the T blocks were expressed as the homopolymeric poly(p-tert-butylstyrene) (PTBS) showed indications of sulfonation when reacted with the sulfonating agent. In our reaction protocol, acetyl sulfate, prepared in-situ in the reaction flask containing the polymer solution, has been used to sulfonate the TST copolymers. This method has been reported previously for sulfonation of homopolymeric polystyrene. In the following sections, the detailed sulfonation and characterization methodologies used in this work are provided first. It is followed by the description of characterization of the reactions and physical properties of the formed ionomers. Features such as morphology development, periodicity in microstructure and variation in solvent uptakes with sulfonation levels in the synthesized block ionomers are discussed.
8.2 Experimental procedures

8.2.1 Materials

Cyclohexane (PRA grade) was purchased from Aldrich, USA. The 1.4 M sec-butyl lithium in cyclohexane was obtained from Aldrich and used without further purification. Styrene and p-tert-butyl styrene were also purchased from Aldrich, USA and purified as needed by passing through an activated alumina column to remove inhibitors and then the styrene or p-tert-butyl styrene was added to a clean, dry round bottom flask filled with nitrogen and fitted with rubber septa and thermocouple. Dibutyl magnesium was added slowly until a persistent yellow/green color formed. This solution was then allowed to stir for a minimum of one hour to react with trace impurities followed by passing this mixture through an activated alumina column to remove impurities. Dichloroethane (DCE) (99.8+%), sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) (98%), acetic anhydride (AA) (99+%) and tetrahydrofuran (99.6%) were purchased from Fisher Scientific, USA and used without any purification.

8.2.2 Copolymer synthesis

To a clean reactor was added a fresh supply of cyclohexane and THF to make a 0.1% solution of THF in cyclohexane and then the desired amount of purified styrene was added. The reaction was initiated by dropwise addition of sec-butyl lithium. Once a persistent yellow color is achieved, the calculated amount of sec-butyl lithium was charged to the reactor to give the desired molecular weight. A period of 30 minutes was allowed to
elapse to permit complete conversion of the styrene, at which time a sample of polystyrene first block was taken and then the desired amount of \textit{p}-tert-butylstyrene was added. After an additional 30 minutes, to allow for complete conversion of the \textit{p}-tert-butylstyrene the reaction was terminated with degassed isopropanol. The contents of the reactor are pumped out under pressure and precipitated into a slightly acidic methanol/ isopropanol mixture. The precipitated mixture is vacuum dried, and stored under refrigeration. Homopolymer of poly(\textit{p}-\textit{tert}-butylstyrene) (PTBS) was synthesized by the same procedure except that no additional blocks were growth at the chain ends.

The synthesized polymers were characterized for molecular weight and polydispersity by size exclusion chromatography with Ultrastyragel Columns of 500, 1000, 10,000 and 100,000 Å porosities in tetrahydrofuran using refractive index and light scattering detectors to determine absolute molecular weights. Compositions were determined by \textit{1}H-NMR analysis using a GE QE-300 NMR. The copolymer had a molecular weight of 182000 Da, where the two T end blocks were 21000 Da and the S midblock was 80000 Da. The polydispersity was 1.006. The PTBS had molecular weight of 47000 Da, which is in a close proximity to the total of two T endblocks in a copolymer chain, and a molecular weight distribution of 1.003.
8.2.3 Block ionomer synthesis

_Sulfonation_

All glassware was thoroughly cleaned and dried prior to use. In each reaction run, 10g of the copolymer was charged to a two-neck round-bottom glass flask. About 180 ml DCE and 10 ml of AA was then charged along with a magnetic stir bob. The AA was added to react with any residual moisture that might have been present in the polymer or in the glassware and would have interfered with the reactions. The side-neck of the flask was connected to a water-cooled condenser capped by a nitrogen line. The middle-neck was connected to an addition funnel that had a pressure-equalization side-arm and a glass stopcock. Liquid reagents were added using this addition funnel in subsequent stages. The entire assembly was inserted in an oil bath kept at a controlled temperature. A slight positive nitrogen pressure was maintained throughout the reaction as its flow was monitored with a bubbler. To minimize moisture entrance into the reaction flask, nitrogen was dried before passing it into the reaction flask.

The copolymer, DCE and AA were stirred till complete dissolution of the polymer occurred. Then the temperature of the oil bath was raised to 50 °C and the solution was stirred for 1 h at this temperature. The quantity of required H₂SO₄ was calculated by varying the molar ratio \( n_{H_2SO_4}/n_S \) (which, once acetyl sulfate is formed is can also be expressed as \( n_{acetyl\ sulfate}/n_S \)) between 0.5 to 4.0, where S stands for polystyrene in the block copolymer. The amount of AA was then calculated by keeping the molar ratio of AA to H₂SO₄, \( n_{AA}/n_{H_2SO_4} \), of 1.15. This amount of AA was added to the solution followed by addition of
H$_2$SO$_4$. The reaction was continued for 96 h at 50 °C followed by precipitation of the product in deionized water (DI). The product based on the achieved level of sulfonation swelled to varying degrees in water on precipitation. At higher sulfonation levels the precipitate made a gel-like material. The above procedure was used for running the control reaction on PTBS by keeping the mole ratio of H$_2$SO$_4$ to AA of 4.0.

**Product purification**

The product purification protocol depended on the level of sulfonation of the copolymer, which in turn was decided by the ratio of $n_{\text{acetyl sulfate}}/n_S$ used. When the ratio was 0.5, the precipitated product was filtered, dried in air and re-dissolved in THF. The solution was loaded in dialysis bags and dialyzed against several liters of deionized water as the conductivity was monitored for equilibration. When the $n_{\text{acetyl sulfate}}/n_P$ was $\geq$ 1.0, the products soaked significant amounts of water making their air drying difficult. They were, hence, filtered and washed with cold and warm DI water several times. They were finally lyophilized to obtain the dry ionomers.

**8.2.4 Ionomer film preparation**

The block ionomer obtained for the $n_{\text{acetyl sulfate}}/n_S$ ratio of 0.5, was dissolved in THF, while all other ionomers were dissolved in a 10:1 mixture of THF and water. The solutions were then poured into the Teflon trays and solvents were allowed to evaporate. For NMR, FTIR and solvent uptake measurements the films were dried in vacuum oven at 40 °C for 12
h in the presence of a drying agent. For thermal analysis both, dried and un-dried, films were used. The sulfonation levels were determined from $^1$H NMR spectra and the samples were labeled as TSTxx, where T stands for the copolymer endblock and S for the midblock. The ‘xx’ represent the degree of sulfonation (DOS). The neat copolymer was represented as TST00. TST00 film was cast from THF and annealed at 135 °C before use to remove any trapped solvent in the glassy blocks.

8.2.5 Sulfonation characterization

8.2.5.1 $^1$H NMR measurements

The deuterated dimethyl (DMF) and deuterated chloroform (CDCl$_3$) were obtained from Cambridge Isotope Laboratories, Inc., Boston, MA. The TST00 and all ionomers were dissolved at room temperature overnight in DMF from freshly opened ampules. The neat PTBS and reacted PTBS were dissolved in CDCl$_3$. The $^1$H NMR spectra of these solutions were recorded using a 300 MHz Gemini 2300 NMR spectrometer. At 300 MHz, 64 scans were taken and peaks were referenced to solvent peaks.

8.2.5.2 FTIR-ATR measurements

Presence of sulfonic acid group was confirmed from FTIR-ATR spectra. The tests were performed on the neat copolymer and ionomer films. The equipment used was Thermo Electron FT-IR with Nexus 470 bench and ATR device was an ORBIT Sampler with
diamond crystal. All FTIR spectra were taken with 128 scans with a frequency resolution of 4 cm\(^{-1}\) between the frequency range 4000-400 cm\(^{-1}\). Peak at 1600 cm\(^{-1}\) due to out-of-plane deformation of ring CH was used to normalize the spectra for variation in film thicknesses.

8.2.6 Thermal characterization

TA-Instruments Thermal Gravimetric Analyzer Q500 was used to determine the thermal stability of TST00 and the ionomers. The samples were heated from ambient temperature to 600 °C with a ramp rate of 5 °C/min under a N\(_2\) atmosphere.

8.2.7 Microstructure characterization

SAXS measurements were performed on a Molecular Metrology SAXS instrument with a sealed-tube source. Cu K\(\alpha\) radiation with a wavelength of 0.154 nm was used. A three-pinhole collimation system produced a spot size at the sample of 700 µm. The raw data were calibrated for the peak position with the standard silver behenate, which has peak position at scattering vector, \(q = 1.076\) nm\(^{-1}\). The sample-to-detector distance was found to be 1.4 m using the above calibration. Each profile was recorded at room temperature over a period of 1 h. The background (similar conditions without any sample) was subtracted from the intensity of the scattered beam. The profiles are represented as a function of magnitude of scattering vector, \(q\), which is related to the scattering angle, \(\theta\). The samples were in the film form as cast from solutions without any annealing and hence retained the moisture absorbed or water
trapped from the casting process, the approximate amounts for which were calculated from 
TGA experiments described above.

8.2.8 Solvent uptake measurements

The TST00 and ionomers in the film form were oven-dried as described above, weighed and then soaked in water in closed vials at room temperature for 24 h, after which 
they were taken out and wiped gently to remove excess solvent and weighed. Temperature of 
water used in these measurements was 30, 60 and 90 °C. Solvent uptake \( U \) was calculated 
by the equation given below after compensating for water content present in the film after the 
drying process as determined from TGA.

\[
U = \frac{\text{Wet film weight} - \text{Dry film weight}}{\text{Dry film weight}} \times 100
\]  

8.3 Results and discussion

The sulfonation of polystyrene either as a homopolymer or in copolymers has been of 
interest for at least a few decades. Several procedures exist for carrying sulfonation reactions. 
A choice of one over the other is decided by the level of sulfonation desired and the control 
need on the reaction. The sulfonation of the polystyrene present as a midblock in a triblock 
copolymer has been reported a few times mainly by using acetyl sulfate as made by 
Makowski’s procedure or by reacting with a TEP:SO\(_3\) complex. The triblocks of similar 
type— TST— are sulfonated here by using acetyl sulfate as a sulfonation agent formed in-
situ in the polymer solution containing reaction flask. The procedure has been reported for sulfonation of polystyrene in literature and is based on the modification of the Makowski’s method. Scheme 8.1. shows the reaction steps in this procedure. The concentration of acetyl sulfate was varied to achieve different DOS. The products obtained were characterized by $^1$H NMR and FTIR-ATR.

The typical spectra for the TST00 and TSTxx ionomer, where sulfonation level ‘xx’ is indicated in % as 15 and 49, are shown in Figure 8.1. The spectra were taken in deuterated dimethyl formamide (DMF) and can be divided into two regions: (a) the aromatic band due to the protons from the aromatic rings and (b) the aliphatic zone coming from the protons in the copolymer backbone and the t-butyl groups on the T units. Three solvent peaks appeared for DMF due to the residual protons from its incomplete deuteration at δ= 2.75, 2.92 and 8.03 ppm. In TST ionomer spectra, an additional sharp peak due to absorbed moisture by the sulfonic acid groups appeared between 3.60 and 4.40 ppm. This peak was seen in all the ionomer samples and shifted to lower magnetic field and became broader, possibly due to increased hydrogen bonding between water molecules, as the sulfonation levels increased. In the aromatic band, while TST00 showed two peaks, TST ionomers showed an additional peak. The peaks are labeled as A (maximum at ~ 7.14 ppm), B (maximum at ~ 6.66 ppm) and C (maximum at ~ 7.60 ppm). In the ionomers, three types of chemical units exist as shown by chemical structures in the figure, viz., non-sulfonated styrene, sulfonated styrene and $p$-tert-butylstyrene units. The poly($p$-tert-butylstyrene) block was not sulfonated as inferred from the explanation provided later. As no control with regards to which styrene units were to be sulfonated was exercised during the reaction, the sulfonated and non-
sulfonated styrene units are supposed to be randomly arranged in the ionomers. The protons contributing to the labeled peaks are indicated by a subscript corresponding to the respective peak.

The peaks A, B, and C are also labeled in Figure 8.2, where the spectrum for all the ionomers and TST00 are plotted in the range 6.0 to 8.0 ppm. Peak A was from the ortho aromatic protons of both the blocks and was seen at the same location for the ionomers and the parent copolymer. Peak B was from the meta protons of both the blocks and the para proton of the T units. On sulfonation, the signal from the meta protons of the sulfonated polystyrene units started appearing as a new peak denoted as peak C in the figure. This assignments match with the previous reports for sulfonated polystyrene and sulfonated block copolymers of the architecture same as TST. The degree of sulfonation (DOS) was calculated based on the known fixed T block content in the copolymer and the integral peak areas of B and C peaks as has been reported in the literature. The DOS values in mol% were used to label the results for the ionomers in this paper. The DOS increased as the ratio, \( \frac{n_{\text{acetyl sulfate}}}{n_S} \), in the reaction increased nearly linearly as shown in Figure 8.3. The presence of sulfonic acid groups was further confirmed by FTIR.

As mentioned above, sulfonation of block copolymers having TST or STS architecture has been performed in the past. In one of the reported procedures, by Yang et al., \( \text{SO}_3:\text{TEP} \) complex was used as a sulfonating agent. The selective sulfonation of the S block was desired and hence to confirm if this was achieved a homopolymeric PTBS was reacted as a control. The PTBS units were seen to get sulfonated by the complex and only
when present along with polystyrene (as one of the blocks in the copolymer) its sulfonation was avoided. The sulfonation occurred at the ortho position of the PTBS units that appeared as a peak at 7.80 ppm in the $^1$H NMR spectrum. To determine conclusively if the T blocks were sulfonated by the reaction procedure we used, similar to Yang et al.’s approach, a control reaction was performed on homopolymeric PTBS. The molar ratio of acetyl sulfate to PTBS of 4.0 was selected, which is same as $n_{\text{acetyl sulfate}}/n_S = 4.0$ as used to obtain the highest DOS of TST copolymer. The reaction product was soluble in chloroform, but not in water indicating that it has either a very low DOS or it remained unaffected during the reaction. In Yang et al.’s work, the reacted PTBS was not soluble in chloroform as would be expected if the aromatic rings were to be sulfonated. Insolubility in water was also reported, which could, again, be due to low levels of sulfonation (27% in their case) as at higher sulfonation levels solubility in water would be expected.

The $^1$H NMR spectra of the untreated and treated PTBS were taken and are shown in Figure 8.4. Both the spectra look similar. In the aromatic zone (6.0–7.2 ppm), peaks resembling peaks A and B as in Figure 8.1 were noted. No peak at 7.8 ppm or at lower magnetic fields (higher ppm) was observed, thus, confirming that the sulfonation procedure did not sulfonate the PTBS units. Based on this observation, it is safe to assume that the T blocks were not sulfonated in the TST ionomers.

The sulfonation of polystyrene blocks was confirmed from FTIR (Figure 8.5). A doublet at 1200 cm$^{-1}$ and a band at 1030 cm$^{-1}$ were seen corresponding to antisymmetric and symmetric stretching vibrations of $SO_3^-$ group.$^{25}$ The intensity of these peaks progressively
increased as the \textit{DOS} increased. The two bands, characteristic of monosubstituted benzene rings, that is, coming from polystyrene rings, appeared at 760 and 698 cm\(^{-1}\) (\textit{cf.} Figure 8.6, peak M and N respectively) as has been reported by Yang et al., in TST00. The former is due to the out-of-plane skeleton bending vibration of the benzene, while the latter is from the out-of-plane bending vibration of the five -CH groups in the benzene ring. These bands provided a check on the sulfonation extends. Their intensities were seen to reduce progressively with increasing \textit{DOS}. The peak at 698 cm\(^{-1}\) has been reported to correlate with the sulfonation degree in literature. Unlike as in the work of Yang and coworkers\textsuperscript{23}, no peak at 1090 cm\(^{-1}\) was seen, however a peak at 907 cm\(^{-1}\) as seen by them was observed. These two peaks, or the latter one as in TST ionomers, were hypothesized to be due to \textit{ortho}-position sulfonation of styrene or \textit{p-}tert-butylstyrene units. Recall that \(^1\text{H} \text{NMR}\) indicates no sulfonation of PTBS in our case. Also, a disubstitution of the styrenic phenyl ring, if were to occur resulting into rings having sulfonic acid groups at ortho and para positions, an additional signal in the NMR of TST ionomers beyond 7.58 ppm should have appeared, which is not observed. Thus, the possibility of sulfonation at the ortho-position in either blocks of TST copolymer, is considered improbable. Also, the peak at about 907 cm\(^{-1}\) was also seen for TST00 in its FTIR spectrum, which later showed no trends in intensity variation on sulfonation, making its assignment questionable to ortho-position sulfonation of the aromatic rings. No attempt was made to quantify the sulfonation levels from FTIR due to the difficulties introduced from presence of absorbed moisture.\textsuperscript{24} The absorbed moisture was evaluated from thermogravimetric analysis.
The weight loss in TST00 and TST ionomers with temperature is shown in Figure 8.7. The TST00 showed a one-stage weight loss starting at 310 °C, which was assigned to the backbone degradation. The significant weight losses for ionomers occurred in four stages as delineated from plots for derivatives of weight loss. A representative curve (DTG49) for TST49 is shown in the figure and four stages of weight losses are also marked appropriately with shades. The temperature ranges for the four stages were 30-175, 200-360, 360-440 and 440-above °C. The first three stages are similar to those reported earlier for endblock sulfonated triblock ionomers. In the 30-175 °C, the loss was from the residual moisture absorbed from surroundings by the sulfonic acid groups. The release of absorbed moisture occurred over an extended temperature range beyond 100 °C due to the strong ionic interaction of the sulfonic acid moieties with water molecules. The moisture contents in ionomers were calculated from the weight loss curves, which showed an increase as the ionic concentration increased. Figure 8.8 shows this variation. In other words, weight loss due to moisture increased as DOS increased, which was anticipated. The loss in 200-360 °C is due to the splitting of sulfonic acid groups. As DOS increased the weight loss in this stage increased. Along with the process of acid group removal from the polymer backbone, the second process of sulfone bond formation from dehydration of sulfonic acid groups and a proton from adjacent phenyl group is anticipated to occur in this temperature range, thereby crosslinking the two phenyl rings. Due to simultaneous occurrence of these two processes in this temperature regime, it is not accurate to calculate the amount of sulfonic acid groups from the degradation curves and hence no attempt was made to do so. In the third stage of weight loss between 360 and 440 °C, the polymer backbone decomposed. The ionomer
backbones degraded at reduced temperature values, as determined from the peak position in derivative plots in this temperature range. At 440 °C, the weight loss was not 100% and char was left in the test pans. This char was from the sulfone-crosslinked polymer. The sulfones are known to have improved thermal stability that explains the residue. Finally beyond 440 °C, in the last stage, the sulfones degraded summing up the weight loss to about 100%.

Polymer membranes made of block ionomers having high ion conductivity and solvent uptake and transport have been the focus of current research, where the phase separated morphologies of these ionomers dictate these properties. With the possibility that the ionomers made in this work will be used as sensors, actuators or possibly as fuel cell membranes, their microstructures were investigated by SAXS. Figure 8.9 shows the SAXS patterns taken for TST00 and the ionomers at room temperature. The TST00 shows a single correlation peak in the range between 0.2 to 0.4 nm\(^{-1}\) indicating the disordered microstructure of the copolymer. The segregation of T and S blocks into their own domains depends on the product of their thermodynamic incompatibility expressed by Flory-Huggins interaction parameter, \(\chi\) and the degree of polymerization, \(N\), of the copolymer. The chemistries of T and S blocks are similar resulting into a low \(\chi\) for the pair that hence a small \(\chi N\) leading to disordered phase separated morphology. As the copolymer was sulfonated to 8%, no change in the SAXS pattern was observed. At the next level of sulfonation of 15 %, the disorder to order transition occurred and an ordered morphology was observed. The solubility parameter of styrene units increases from 9.1 before sulfonation to about 16.6 (cal.cm\(^{-1}\))\(^{-1/2}\) afterwards, thus, indicating the cause for an increased repulsion between the sulfonated S blocks and the T endblocks for which the solubility parameter stays at about 8.1 (cal.cm\(^{-1}\))\(^{-1/2}\). The increased
repulsion increased the segregation tendency between the blocks that then formed a more ordered microstructure. Similar disorder-order transitions have been reported previously in block ionomers, though in most cases ionomer molecular weights were significantly lower than used in this work.

The ionomer TST15 shows distinct scattering intensity maxima located at the wavevector positions: $q^*$, $\sqrt{3}q^*$, $\sqrt{4}q^*$ and $\sqrt{7}*$, where $q^*$ represents the location of the first—principal—peak. These locations indicated that the morphology consists of hexagonally packed cylinders dispersed in the matrix. Based on the volume fractions of the blocks in the parent copolymer, we suspect that the T blocks make the cylinders that are embedded in the sulfonated S matrix. The TEM studies are underway to confirm this. The appearance of three higher order peaks indicate that the long range order was present in the sample. The TST15 film was cast from a mixture of THF and water mixed in a 10:1 ratio, whereas TST00 and TST08 were cast from THF. Though the possibility that a change in solvent induced the ordering of the microphases, as has been reported in previous studies, and resulted into well-defined morphology in TST15 cannot be ruled out, it is highly unlikely considering the observed similarity of its principal SAXS peak with that for TST00 and TST08. Further studies are required to ascertain this. A strong evidence for long range order in microphase structure as DOS increased to 37% in TSTS37 was also seen from the SAXS pattern. However, in this case now, the principal peak shifted to lower scattering vector and the peak locations were $q^*$, $1.3q^*$ and $1.6q^*$. Two more peaks are also seen (indicated in the Figure), whose peaks locations are difficult to assign due to the noise in the data. Based on this available SAXS data, the microstructure cannot be assigned with certainty. The TEM
studies are underway to determine the microstructure. Nonetheless, it is likely that TST37 had a different morphology than TST15 with a significant long-range order. Recall that TST15 and TST37 were cast from the same solvent, THF+water mixture, which eliminates the possibility of solvent inducing a morphological transition. This transition can possibly be explained based on the increased volume fraction of the midblock on sulfonation as polystyrene has a molar volume of 99 cm$^3$. mol$^{-1}$ before sulfonation and 130 cm$^3$. mol$^{-1}$ afterwards. Increase in volume occupied by the midblock increases the curvature in the endblock domains changing them from cylinders to spheres. Similar results for morphological transitions have been reported by Park et al.$^{6}$ for poly(styrenesulfonate-$b$-methylbutylene) (PSS-PMB) block copolymers with molecular weights much lower than for TST ionomers. In their case, a transition from disordered to gyroid to lamellae to inverted HPL phases were seen as the volume fraction of PSS increased with sulfonation. The other explanation for the observed transition could also come from the matrix swelling from absorbed moisture which increased as DOS increased leading to a morphological transition. Note that the explanations given here remain to be largely hypothetical as this and other reports, which have offered similar arguments, do not provide any firm evidence confirming them. There are also systems where the morphological transitions were explained based on completely opposite hypotheses of volume densification of ion containing domains due to formation of ionic aggregates. One such example is a companion system consisting of midblock sulfonated poly(styrene-$b$-butadiene-$b$-styrene) that we recently investigated, the results for which are presented somewhere else.
When the sulfonation level increased to 49% in TST ionomers, two higher order peaks after the principal peak were seen in the SAXS pattern with locations at 1.50q* and 2.55q* that do not correspond to any conventional block copolymer morphologies. The higher order peaks were not observed. The observed peaks were less well-defined compared to ionomers discussed above indicating a reduced periodicity in the microstructure. The width of the principal peak increased suggesting the increased inhomogeneity in the phases and shrinking of micelle sizes. The principal peak shifted further to lower vector values compared to TST37 that related to increased interdomain spacing, which agrees well with the above argument of increase in volume fraction of the midblock on sulfonation. The reduced periodicity could be due to the formation of ionic aggregates, which due to their increased number density at higher DOS, affect the segregation between the endblocks and midblocks.

The DOS not only affected the microstructure but also the solvent (water) uptakes (Figure 8.10). As DOS increased, uptake increased. The uptake also increased as the temperature of the water was increased. All ionomer films remained intact and mechanically handleable after swelling.

8.4 Conclusions

Unlike most reports on sulfonated linear triblock copolymers, where the endblocks are sulfonated, midblock sulfonated TST copolymers referred to as block ionomers, were prepared successfully. The two T endblocks remained unaffected in the sulfonation procedure using acetyl sulfate. The reaction scheme is a mild procedure, known from
previous studies, used for polystyrene sulfonation and has been reported not to affect the chain length when the degree of polymerization was < 6000, as was the case for the TST copolymer. A systematic variation in sulfonation was achieved by varying the concentration of acetyl sulfate. The maximum DOS of 49% is reported here, though higher ionic contents, up to 73%, were also achieved. The increase in DOS was discerned from $^1$H NMR and FTIR. The variation in DOS clearly reflected in thermal behavior of the ionomers. The ionomers showed disorder-order transition for TST15 determined from the SAXS pattern that corresponded to hexagonally packed cylinders. As the DOS increased to 37%, likely an order-order transition occurred, followed by less ordered system at 49%, which was assigned to the interference caused to the microphase separation process from the formation of ionic aggregates. The ionomer films swelled in water with varying uptakes systematically increasing with DOS and the temperature of the solvent. The films retained mechanical integrity at all DOS and water uptakes.

8.5 Acknowledgments

The authors would like to thank Prof. Bruce M. Novak, Department of Chemistry, North Carolina State University, NC, and Prof. Robert Weiss, College of Polymer Science and Polymer Engineering, University of Akron, OH for their constant advice and Prof. Christopher B. Gorman, Department of Chemistry, North Carolina State University, NC, for providing access to his research facilities for this work.
Scheme 8.1 Schematic for sulfonation reaction. The acetyl sulfate forms in-situ during the reaction and then reacts with the S block of the TST copolymer.
Figure 8.1 Typical $^1$H NMR spectra of neat TST denoted as ‘00’ and block ionomers with $DOS$ indicated as ‘15’ and ‘49’. The solvent peaks are labeled. The aromatic band and the aliphatic bands are labeled. The monomer units that contribute to the spectra are also shown with the subscripts that match with the corresponding peaks (labeled). All spectra were taken in DMF. The curves are shifted vertically for convenience.
Figure 8.2 The $^1$H NMR of TST00 and all ionomers in 6.0-8.0 ppm range. Peaks are labeled as in figure 8.1.
Figure 8.3 The DOS (connected by a linear fit) calculated based on the polystyrene content in the ionomers as a function of sulfonating agent’s concentration.
Figure 8.4 The 1H NMR of neat homopolymeric PTBS and reacted PTBS (labeled) taken in CDCl₃. The similarity in peaks between 6.0 and 8.0 ppm in the spectra indicated that PTBS was not affected in the sulfonation reaction.
Figure 8.5 FTIR-ATR spectral scans for TST00 and all ionomers TSTxx (labeled with number indicating DOS). The lines correspond to the wavenumbers (marked) and indicate the peaks that appear after sulfonation of TST. The scans are shifted vertically for clarity.
Figure 8.6 Expanded spectra between 400 and 1000 cm\(^{-1}\) for the spectra shown in Figure 4.

Variation in intensities of the labeled peaks indicated sulfonation levels.
Figure 8.7 Thermal behavior of TST00 and select ionomers TSTxx (labeled with numbers indicating DOS). The dotted line is a derivative of the weight loss with temperature for TST49 (labeled as DTG49). The different stages of weight loss are shown in shades.
Figure 8.8 The moisture contents in the ionomers due to their hygroscopic nature as a function of DOS as determined from TGA. As cast films (solid circles) and oven-treated films (solid diamonds).
Figure 8.9 SAXS patterns for TST00 and block ionomers. The arrow heads indicate the location of peaks.
Figure 8.10 Water uptakes by ionomers as DOS varied. Uptakes at two different temperatures are shown: 30 °C (open diamonds), 60 °C (filled triangles) and 90 °C (open circles).
8.6 References


9 Conclusions

Thermoplastic elastomer gels of all-acrylic block copolymers having different molecular weights and block compositions with a high boiling midblock selective solvent, DOP, were demonstrated as dielectric electroactive polymers that actuated at reduced electric fields than the conventional dielectric elastomers (DEs) and with no-prestrain requirements. The prestrain is known to affect the actuator performance by causing failure from stress relaxation of the strained DE with time and to necessitate the need for bulky and heavy frames to hold the prestrain in place, thus, adding to the weight of the device. The gels investigated differed in morphologies dictated by the copolymer compositions and concentrations. Two morphologies were clearly assigned to these gels from SAXS, viz. cylindrical and spherical. For some compositions the morphologies could not be discerned from the SAXS patterns, which were then designated based on the mechanical behavior of these gels. The main criterion used was the presence and prominence of Mullin’s effect, reported for the first time, to our knowledge, in solvated triblock copolymer gels. Cylindrical morphologies showed significant Mullin’s effect, while the spherical ones did not. The morphological features affected the actuation performance. The cylindrical morphologies showed lower actuation at breakdown, higher breakdown fields, higher energy densities and lower coupling efficiencies than the spherical morphologies. These observations indicated that morphology is an important parameter that must be considered in designing a DE, which can be used in tuning the (electro)mechanical behavior.
The concept of using a midblock solvated block copolymer was extended, also for the first time, to design an ionic polymer metal-composite (IPMC)—a different type of electroactive polymer than the DE. The actuation mechanism of IPMCs is totally different than for the DEs. The material design proved to be very versatile facilitating facile fabrication of the actuators that showed high bending actuations and excellent tunability in actuation deflections, directions and rates. The block copolymer had five blocks with the central block having sulfonic acid groups and, hence, was a 'block ionomer'. The ionomers of this type can be used to tune the morphology of the membrane due to their inherent property of undergoing microphase separation forming distinct domains of respective blocks. Morphology is known to directly influence properties such as ion/solvent transport and solvent uptakes that then dictate IPMC actuation performance. With the intention to facilitate this tunability, two synthetic strategies were explored to design new block ionomers by sulfonating midblocks in triblock copolymers. Midblock-sulfonated block ionomers have been scarcely explored in the literature and are challenging to synthesize due to the desired selectivity in sulfonating a specific block without affecting the others.

Two copolymers, poly(styrene-\textit{b}-butadiene-\textit{b}-styrene) and poly[(\textit{p}-\textit{tert}-butylstyrene)-\textit{b}-styrene-(\textit{p}-\textit{tert}-butylstyrene)], were sulfonated to introduce ionic groups in the midblock. The degrees of sulfonation (\textit{DOS}) of the ionomers were successfully varied by changing the concentration of the sulfonating agents. The ionomer microstructures were highly tunable as morphological transitions from one type to the other were seen. Transitions of disorder-order, order-order and order-reduced order were observed. The block ionomers swelled by absorbing solvents to varying degrees depending on their \textit{DOS} and retained their mechanical
integrity suggesting that they could be the potential materials for several applications such as IPMCs, water purification membranes, ion exchangers etc. The synthetic strategies used in this work, can be extended for sulfonation of block copolymers having different block compositions and sizes. These features can then additionally be used to tune the microstructures and hence the subsequent properties influenced by them.
10 Future work

In this work, Mullin’s effect has been reported to exist in triblock copolymer gels. To our knowledge, this is the first ever report indicating this observation. The effect can be explored in details along with the morphological characterization by TEM and SAXS to determine the microstructure evolution under the applied strain. The morphology of block copolymer gels also was seen to affect the actuation behavior. The observation that breakdown field was influenced by the presence of cylinders against the spheres require more investigation to establish the mechanism responsible for this behavior.

The pentablock ionomer showed an excellent actuation behavior as IPMCs. The question of how a change in solvent induces a directional change in deformation needs to be answered. The answer is likely hidden in the solvent interaction with the ionomer or the mobile ions solvent or in electrode chemistry happening at the silver electrodes that needs further exploration. The IPMC performance can be improved by fabricating electrodes from materials such as platinum (no silver), gold or from ruthenium based compounds. The electrode fabrication and properties are known to influence the actuation behavior and hence would comprise very interesting avenues for future studies. The other aspect with regards to membrane material is the chemistry and composition of the block ionomer. The block lengths, composition and number of blocks can be varied to control the morphologies that would enhance the ion/solvent transport properties and hence the actuation.

Two synthetic strategies to obtain midblock-sulfonated SBS and TST ionomers have been explored in this work and were found to be extremely successful in systematically
varying the degrees of sulfonation (DOS) and inducing morphological transitions and periodicity in the microstructure. Robust ionomers of this type can be synthesized by simply varying the ionomer block sizes, composition and molecular weights for use in several applications such as fabricating IPMCs, manufacturing healthcare products, etc. Varying these features can also help in tuning the microstructure that is known to affect several physical, transport and mechanical properties.

Phase behavior of block ionomers as a function of ionic contents remains unclear and detailed molecular modeling should be undertaken to shed light on this aspect. Unlike the current available models for modeling block copolymers, the new models should incorporate the ionic and dipolar interactions seen in ionomeric chains to predict their compatibility with the other blocks in a block ionomer. The understanding achieved through this modeling will be useful in designing novel block ionomers for applications such as fuel cells and IPMCs. In this dissertation, midblock-sulfonated SBS and TST ionomers were successfully synthesized and characterized for their chemistry, thermal behavior and morphological properties. As a next step, evaluation of their ion/solvent transport properties when swollen with solvents and their correlation to the microstructure should be performed. The correlations will help in tuning morphology to obtain improved performance. Some of the important applications for which the synthesized block ionomers can be explored include protein/water purification and use as ion-exchangers. For these applications, the block ionomer webs can be made from electrospinning that can provide extremely large surface area for protein/ion-exchange.
Appendix A

Electroactuation of Solvated Triblock Copolymer Dielectric Elastomers: Decoupling the Roles of Mechanical Prestrain and Specimen Thickness

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Dielectric elastomers (DEs) constitute a class of electroactive polymers that are becoming increasingly important as lightweight and mechanically robust replacements for conventional transducers and actuators. Due to their inherent cycling resilience, they also show tremendous promise as energy-harvesting media, as well as smart sensors and microfluidic devices. Recent studies have demonstrated that DEs composed of midblock-solvated triblock copolymers exhibit attractive electromechanical attributes such as giant electroactuation strains at relatively low electric fields at high conversion efficiency. Moreover, the properties of these systems, which are readily processable, are highly composition-tunable, which makes them ideal candidates for a detailed study of the coupling between initial specimen thickness and mechanical prestrain, which is frequently used to reduce specimen thickness prior to actuation to lower the voltage required to achieve

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electroactuation. Conventional wisdom based on the notion of an ideal DE indicates that electroactuation should only depend on pre-actuation specimen thickness, but we report results that unequivocally indicate a more detailed material/process description is required.

1. Introduction

While a wide variety of materials are capable of changing shape or size in response to an external stimulus such as temperature, chemical environment or electromagnetic radiation,[1] electroactive materials are of general and growing interest because of their intrinsic ability to respond to an external electrical stimulus.[2] By doing so, they can serve as transducers or actuators by directly converting electrical energy to mechanical work. Recent mechatronic studies by Anderson and co-workers[3] have demonstrated that such materials provide a viable route to biomimetic tactile sensing. Of the various types of electroactive materials presently available (e.g., shape-memory alloys[4] and electroactive ceramics[5]), electroactive polymers (EAPs) show the most promise for widespread use in emerging technologies that include (micro)robotics, microfluidic devices, flat-panel speakers, active video displays, and responsive prosthetics.[6] Unlike, for example, cumbersome, energy-inefficient, heavy and slow mechanical (i.e., hydraulic or pneumatic) actuators or expensive and fragile ceramic actuators, EAPs are lightweight, inexpensive, scalable, and mechanically resilient. Moreover, they can be remarkably energy-efficient and exhibit fast response times. These materials are broadly classified as either electronic or ionic on the basis of their mechanism of actuation, and electronic EAPs are further categorized as either electrostrictive or electrostatic. Although electrostrictive EAPs such as poly(vinylidene fluoride) (PVDF) and its copolymers have received considerable attention[7] due to the large forces that they can generate upon
electroactuation, only electrostatic EAPs such as dielectric elastomers (DEs) are considered further here. These EAPs, which exhibit electromechanical properties most closely resembling those of skeletal muscle, tend to possess an elastic network that is capable of (i) achieving large deformations during electroactuation and (ii) returning to its original size and shape upon recovery. For this reason, conventional DEs consist of chemically cross-linked homopolymers, although recent studies have shown that block copolymers that form physically cross-linked and highly elastic networks constitute suitable, if not superior, alternatives.

Block copolymers consist of two or more long, contiguous and chemically dissimilar polymer chains that are covalently linked together to form a single macromolecular surfactant. As surfactants, these copolymers are capable of spontaneously self-organizing into a wide variety of nanostructures or modifying the thermodynamic nature of surfaces or interfaces. Thermoplastic elastomeric triblock copolymers composed of glassy or semicrystalline endblocks and a rubbery midblock are further capable of forming supramolecular networks of bridged midblocks that connect neighboring endblock-rich microdomains, which serve in this capacity as physical cross-links. Addition of a midblock-selective, low-volatility solvent to a triblock copolymer preferentially acts to swell the copolymer midblocks and can, depending on the solvent concentration, yield a highly elastic network capable of achieving uniaxial tensile strains in excess of 2000% before failure. We have recently demonstrated that, as DEs, selectively swollen triblock copolymers can attain giant electroactuation strains (≈ 300% on an area basis) at relatively low electric fields (< 20 kV/mm) and exhibit high electromechanical efficiencies (> 90%) in
the process. This materials design platform is completely general and extends to triblock (as well as higher-order multiblock) copolymers and appropriately selective solvents differing in chemistry, composition and molecular weight.\textsuperscript{[16]}

To reduce the electric potential required to achieve electroactuation of these copolymer, as well as homopolymer-based, systems (for safety and implementation reasons), specimen films are routinely prestrained to decrease the film thickness.\textsuperscript{[17]} A nominal electric field is then expressed as the applied potential divided by the film thickness after mechanical prestrain. Such normalization is considered sufficient to achieve reproducibility for comparative purposes, but our findings indicate otherwise. In this study, we provide evidence that the initial film thickness, in addition to the film thickness after prestrain, must be independently taken into account during electromechanical testing. This parametric coupling may explain inconsistencies reported in the literature and further elucidate the fundamental mechanism of electroactuation in EAPs.

2. Actuation Mechanism

As schematically depicted in Fig. 1, a DE can be envisaged as a compliant capacitor. It consists of a thin elastomeric film sandwiched between two compliant electrodes. When a potential is applied across the electrodes, the resultant electric field induces attraction between the oppositely charged electrodes and repulsion of like charges along the same electrode, thereby generating a compressive Maxwell stress ($\sigma_M$) that acts normal to the film surface. Since the process is isochoric, the elastomer and the compliant electrodes
concurrently expand laterally. The change in the lateral surface area of the electrode (ΔA) relative to the initial electrode area (A₀) is recorded as the actuation strain (s_{act} = ΔA/A₀). When the field is removed, the elastomer returns to its original size and shape, ideally without extensive non-recoverable deformation, even upon cycling. The charging current of such a capacitor is low. If the leakage current is negligible, no further energy is required to maintain the actuation strain. By tuning the mechanical properties so that viscous loss is minimized, devices constructed around these DEs can be extremely efficient. According to the ideal DE model,[17a,18] the magnitude of \( \sigma_M \) acting in the perpendicular (z) direction of the specimen is given by

\[
\sigma_M = \frac{1}{A} \frac{dU}{dz}
\]  

(1)

where A is the expandable surface area of the electrode, and U is the applied electrostatic potential. Since the arrangement of a DE is identical to that of a parallel plate capacitor,

\[
U = \frac{1}{2} \frac{Q^2}{C}
\]  

(2)

where Q is the charge on the capacitor place, and C is the capacitance defined by

\[
C = \frac{\varepsilon A}{z}
\]  

(3)

Here, \( \varepsilon \) denotes the permittivity of the medium. Substitution of Eqs. 2 and 3 into \( dU/dz \), followed by simplification and algebraic rearrangement, yields

\[
\sigma_M = \frac{1}{\varepsilon A^2} \frac{Q^2}{A^2}
\]  

(4)

Since the electric field (E) between the compliant electrodes can be written as
\[ E = \frac{Q}{\varepsilon A}, \]  
\[ \sigma_M = \varepsilon E^2 \]  
\[ s_z = (1 + s_{\text{act}})^{-1} - 1 \]  

The accompanying transverse strain resulting from this stress is denoted by \( s_z \) and is determined from \( \Delta z/z_0 \), where \( \Delta z \) is the change in film thickness and \( z_0 \) is the initial film thickness shown in Fig. 1. The transverse strain and (in-plane) area actuation are related through

Most DEs of contemporary interest are hyperelastic and exhibit large actuation strains (in excess of 100%). In the analogous mechanical case, semi-empirical constitutive relationships, such as the generalized Mooney-Rivlin, Yeoh or Ogden models,\(^{[19]}\) must be used to relate stress to strain.

It is clear from Eq. 6 that the magnitude of \( \sigma_M \) developed during actuation, and thus the level of actuation achieved, can be increased by increasing the permittivity of the elastomer (given by the product of the dielectric constant, \( k \), and the permittivity of free space) and/or the applied electric field. Since the electric field is likewise given by \( U/z \), voltage requirements to achieve a target \( \sigma_M \) level can be reduced by decreasing the thickness of the elastomer film. As mentioned earlier, this is readily accomplished by mechanically prestraining a specimen film prior to actuation. Although specimens are routinely subjected to equibiaxial prestrain, they may also be prestrained uniaxially, since highly anisotropic strains can be used to promote preferential actuation in specific directions.\(^{[20]}\) While the
effect of prestrain on the dielectric constant of a given elastomer is still open to debate, studies have shown experimentally\textsuperscript{[21]} and theoretically,\textsuperscript{[22]} on the basis of thermodynamic stability criteria, that prestrain improves the breakdown field (also referred to as the dielectric strength) of the elastomer. Prestrain is particularly beneficial in materials that undergo strain hardening during deformation. In this case, the required Maxwell stress to trigger so-called "pull-in" failures, which develop due to a positive feedback loop between the applied electric field and the instantaneous film thickness, increases, thereby leading to thinner films and eventual dielectric breakdown.\textsuperscript{[23]} We hasten to point out at this juncture that not all DEs require prestraining, which is undesirable for commercial implementation. Prestraining requires a frame support that adds to the size and weight of the actuator, and it can degrade the desired properties of the DE as the DE undergoes prolonged stress relaxation over long periods of inactivity. Recent studies by Vargantwar et al.\textsuperscript{[16]} have demonstrated that thermoplastic elastomer systems derived from selectively-swollen acrylic triblock copolymers can achieve actuation strains greater than 100% without prestrain. Likewise, Ha et al.\textsuperscript{[24]} have shown that prestrain can be effectively locked-in (so that it can be avoided during application) through the addition of a second cross-linkable species that forms a secondary network in a chemically cross-linked elastomer. Electroactuation area strains attained in materials produced in such fashion exceed 200%. 
3. Results and Discussion

3.1. Mechanical Behavior of SEBS/MO Systems

Figure 2a displays a representative stress–strain curve measured in quasi-static compression from a poly[styrene-\(b\)-(ethylene-\(co\)-butylene)-\(b\)-styrene] (SEBS) triblock copolymer selectively solvated with an aliphatic-rich oil (the details of which are provided in the Experimental Section) at a concentration of 30 wt% copolymer. For comparative purposes, we presume here that the stress induced upon mechanical compression (\(\sigma_C\)) emulates the Maxwell stress (\(\sigma_M\)) that develops upon electroactuation. Although the two modes of deformation are clearly related, differences may arise because of existing boundary conditions, as well as field-induced changes in material properties. Included for comparison in Fig. 2a is a biaxial tensile stress–strain curve that has been generated by transforming a quasi-static uniaxial tensile stress–strain curve through the use of the Ogden hyperelasticity model.\[^{25}\] In this case, the true (Cauchy) mechanical stress measured under uniaxial tension (\(\sigma_u\)) as a function of displacement, or stretch (\(\lambda = L/L_0\), where L is the specimen length and the subscript 0 denotes initial conditions), can be fitted to an expression of the following form:

\[
\sigma_u = \sum_{k=1}^{m} u_k \left( \lambda^{\alpha_k} - \lambda^{\frac{\alpha_k}{2}} \right)
\]

where \(u_k\) and \(\alpha_k\) are adjustable parameters, and \(m\) is the number of elements chosen (typically 2 or 3, depending on the complexity of the stress–strain relationship). These
parameters are subsequently employed to compute the equibiaxial Cauchy (true) stress ($\sigma_b$) as a function of tensile strain ($s$, where $s = \lambda - 1$) in Fig. 2a from

$$\sigma_b = \sum_{k=1}^{m} 2u_k \lambda^{a_k} - \lambda^{-2a_k}$$

(9)

According to McKenna and co-workers,\textsuperscript{[26]} the true biaxial stress in the limit of isotropic behavior can be converted into an equivalent compressive stress by applying the following transformations:

$$\lambda_c = \frac{1}{\lambda_b}$$

(10a)

and

$$\sigma_c = \sigma_b$$

(10b)

The mechanical moduli extracted from compressive and biaxial tensile deformation data ($Y_C$ and $Y_b$, respectively) are presented as functions of copolymer concentration (C) in Fig. 2b. Values of $Y_C$ are consistently lower than those of $Y_b$, which indicates that the two moduli provide different, but complementary information regarding the mechanical attributes of the copolymer network. Previous independent studies\textsuperscript{[27]} have demonstrated that the dynamic elastic shear modulus ($G'$) or plateau shear modulus ($G$) scales as $C^n$, where the scaling exponent $n$ depends on the chain entanglement regime. If the network-stabilizing glassy micelles are sufficiently separated at low C, their coronal midblocks do not overlap, and the unentangled micelles effectively behave as discrete beads on an elastic network formed almost exclusively by bridged midblocks. In this Rouse limit, $n = 1$. At higher C, the micelles lie closer together and entangle, resulting in higher values of n due to entanglement
contributions to the modulus. Values of $n$ have been previously reported to lie between 2 and 2.5 for a wide variety of triblock copolymers swollen with different midblock-selective solvents. As pointed out elsewhere,\textsuperscript{[28]} these values are numerically comparable to those predicted by de Gennes\textsuperscript{[29]} for an entangled homopolymer in a good (2.25) or $\theta$ (2.33) solvent. Values of $n$ determined from the power-law regressions included in Fig. 2b are 2.10 (compression) and 1.67 (biaxial tension), the former of which agrees modestly well with the prior results discussed above. This comparison indicates that the quasi-static mechanical (and, by inference, electromechanical) properties of DEs derived from selectively-solvated triblock copolymers can be ($i$) interpreted in terms of established polymer network relationships and ($ii$) tailored by changing copolymer concentration. The principal advantages of copolymer-based DEs (whose network develops as a consequence of thermodynamic interactions) over homopolymer-based DEs (whose network forms by stochastic chemical reaction) have been observed in terms of low viscous losses and stability.\textsuperscript{[15a,15b,15d]}

3.2. Electromechanical Properties of SEBS/MO Systems

3.2.1. Dielectric Behavior

As pointed out earlier, Eq. 6 reveals that, in the case of an ideal DE, the Maxwell stress attained during electroactuation is proportional to the permittivity of the DE under isoelectric field conditions. Measurements of the dielectric constant ($k$) of SEBS/MO solutions varying in copolymer concentration from 5 to 30 wt% confirm little variation, with $k$ ranging from 1.97 to 2.20. This is not surprising since values of $k$ for the SE and EB copolymer blocks and
the oil are all very similar on the basis of their chemistry. Although this range is considerably lower than the values of k previously reported for acrylic[^30] and siloxane[^31] DEs capable of large actuation strains, an important and distinguishing characteristic of the present SEBS/MO elastomers is that k is nearly independent of frequency between 100 Hz and 1 MHz primarily due to the absence of discernible chain relaxation in the physically cross-linked network. This is not the general case for homopolymer-based DEs in which k decreases steadily with increasing frequency due to segmental relaxation.[^30] In this regard, the chemically cross-linked DEs are anticipated to experience a higher compressive stress than copolymer-based DEs during electroactuation, but they exhibit a technological limitation that the copolymer-based DEs do not. Material-specific factors must also be considered in conjunction with k to fully understand electroactuation behavior.

3.2.2. Actuation Behavior

In Figs. 3-5, actuation strain (expressed on an area basis, as described in Section 2) is provided as a function of the nominal electric field (calculated from the thickness of each specimen film after applying prestrain but before actuation) for SEBS/MO systems varying in copolymer concentration from 5 to 30 wt%. These three sets of figures correspond to applied prestrain values of 100, 200 and 300%, respectively. At each prestrain level, the role that initial film thickness plays on the extent of electroactuation is interrogated (see panels a-c in Figs. 3 and 4, and panels a-d in Fig. 5). Data for films measuring 3 mm thick (Fig. 5d) are not displayed at the lower prestrain values of 100 and 200% (in Figs. 3 and 4, respectively) because the measured actuation levels are insignificant up to the maximum
voltages used in the study (13-17 kV). Cursory examination of these curves immediately establishes that, at constant prestrain and initial film thickness, the copolymer concentration plays a crucial role in governing the electromechanical response of these systems, which is consistent with their mechanical properties discussed earlier and previously reported\textsuperscript{[15]} observations. Although the level of prestrain and the initial film thickness influences the magnitude of actuation, the operational curves displayed in Figs. 3-5 establish that the non-linear properties of SEBS/MO DEs are similarly, but not identically, affected. At a given electric field, materials that are softer and possess a low copolymer concentration tend to exhibit some of the highest actuation strains after a large prestrain (cf. Fig. 5). Closer examination of the trends apparent in each figure (at constant prestrain) reveals that both copolymer concentration and initial film thickness can have a nontrivial effect on the maximum actuation achieved at dielectric breakdown. In Fig. 5c, for instance, the maximum actuation obtained increases with increasing copolymer concentration (and material stiffness according to Fig. 2b), whereas the opposite trend is evident in Fig. 5d. The data in each figure therefore display material- (concentration), as well as process- (thickness), dependent actuation properties. The remainder of this study focuses on determining the extent and cause of this coupled dependence.

To better understand the electroactive response of the present materials, we re-analyze the actuation results presented in Figs. 3-5 within an electromechanical compression framework. By using Eq. 6 for the Maxwell stress and the definition of the transverse strain, we convert the actuation–field curves in these figures to electromechanical stress–strain curves that are analogous to purely mechanical compressive stress–strain responses. A
representative series of such electromechanical data extracted from Figs. 3c, 4c and 5c is displayed for SEBS/MO systems prepared at an initial film thickness of 1.8 mm and subjected to mechanical prestrain levels of 100, 200 and 300% in Fig. 6. In calculating the Maxwell stresses, true, not nominal, electric field values (determined from the instantaneous voltage and film thickness) are used. Here, the resulting compression (and, hence, electric field and film thickness) is presumed to be uniform throughout the entire (circular) active area, although we recognize that the material squeezed laterally acts against a restorative force originating from the undeformed surrounding material. Moreover, k is considered independent of increasing prestrain or compression during electroactuation so that the values of k measured experimentally under static conditions remain applicable. Although measurements of k from stretched specimens have not been performed during the course of this investigation, this simplifying assumption is believed to be valid due to the absence of discernible relaxation in strained SEBS/MO systems even in the hyperelastic regime at ambient temperature.\cite{15c} At low strain levels in Fig. 6, each DE is observed to display linear behavior, in which case the electromechanical stress–strain curve can be represented by a straight line. Beyond the linear region, strain hardening develops, which has direct implications regarding the electromechanical stability of the DE system according to Zhao and Suo.\cite{32}
3.2.3. Electromechanical Modulus

The initially linear portion of electromechanical curves such as those presented in Fig. 6 can be analyzed in analogous fashion as mechanical stress–strain curves to extract a corresponding electromechanical modulus ($Y_E$) from the slope. Within the limitations of the assumptions discussed above, we propose that this previously unused means of analysis provides a precise and systematic metric by which to compare the electromechanical performance of DEs, unlike some ultimate properties that are sensitive to the presence of defects and impurities, as well as slight, but non-negligible, variations in specimen preparation (e.g., initial thickness, as examined in this study). Values of $Y_E$ measured from SEBS/MO systems at different copolymer concentrations and evaluated at equibiaxial prestrain values of 100, 200 and 300% are displayed as a function of $C$ in Fig. 7. Each point in this figure corresponds to the average of moduli from specimens differing in initial thickness. Also included for comparison in Fig. 7 are the $Y_C$ data previously obtained from purely mechanical measurements (cf. Fig. 2b). As in Section 3.1, values of $Y_E$ can likewise be fitted to a power-law equation, thereby verifying the existence of an analogous scaling relationship of the form $Y_E \sim C^n$. Regression of all the electromechanical moduli displayed in Fig. 7 yields $n \approx 2.00$ within experimental scatter. Recall that, for $Y_C$, $n = 2.10$, which implies that the mechanism responsible for the response of these copolymer-based systems to both mechanical and electromechanical deformation is similar, if not identical. It is important to recognize, however, two distinguishing features of Fig. 7: (i) the values of $Y_E$ are consistently larger than $Y_C$, and (ii) $Y_E$ increases with increasing prestrain value. An increase in $k$ caused by prestraining could account for this apparent increase, but the nearly order of
magnitude increase in $Y_E$ from no prestrain ($Y_C$) to 300% prestrain due to such a prestrain-induced change in $k$, while remaining open to experimental interrogation, is considered unrealistic. Instead, we largely ascribe the systematic increase in $Y_E$ to stiffening of the copolymer midblocks comprising the network as they are subjected to mechanical prestrain prior to electroactuation. Purely mechanical studies\cite{15c} of swollen triblock copolymers, however, show the opposite behavior, viz., the mechanical modulus has been measured to decrease upon biaxial stretching. This disparity further suggests that caution must be exercised in equating mechanical and electromechanical attributes.

Due to their comparable functional dependence on copolymer concentration, it is apparent that all the values of $Y_E$ displayed in Fig. 7 can be readily normalized to cluster around a master curve. More importantly, though, division of the stress values in electromechanical stress–strain curves such as those shown in Fig. 6 by their corresponding electromechanical modulus results in collapse of the curves acquired at different copolymer concentrations onto a single master curve at each prestrain level, an example of which is included at an initial film thickness of 1.8 mm in Fig. 8. Such remarkably uniform electromechanical response indicates that the underpinning mechanism responsible for deformation during electroactuation is, for the most part, independent of copolymer concentration over the concentration range examined here. Since one of the principal objectives of this study is to establish the roles of initial specimen thickness (prior to prestrain) and applied prestrain on electromechanical behavior, we now consider electromechanical stress–strain curves acquired from a SEBS/MO system at an arbitrarily fixed copolymer concentration of 25 wt% and variable initial thickness and prestrain values.
in Fig. 9. Results obtained from systems at other copolymer concentrations are qualitatively similar and are not included here for that reason. Since all the curves provided in each panel of Fig. 9 lie on top of each other within experimental uncertainty, we conclude that film thickness does not strongly influence the nature or shape of the material response to electroactuation, which is also the case for mechanical compression insofar as a film is not sufficiently thin so that the inserted probe is affected by the underlying substrate. Similar comparison of Figs. 9a-c for which prestrain varies from 100 to 300%, however, reveals that the effect of applied prestrain on electroactuation promotes different electromechanical responses and thus cannot be neglected.

3.2.4. Dielectric Strength

Although the significance of initial film thickness is not evident in the master curves shown in Fig. 9, it can impact the ultimate (i.e., dielectric breakdown) properties at which maximum actuation is achieved. This effect has been largely ignored in reports of DE performance involving chemically cross-linked homopolymers or physically cross-linked copolymers primarily because ultimate properties evaluated at failure are often stochastic. It is therefore reasonable to expect variability in these properties, one of which is the electric field corresponding to maximum actuation (i.e., the dielectric strength). In Fig. 10, the effect of mechanical prestrain on dielectric strength is presented as functions of copolymer concentration (0.10 in Fig. 10a and 0.30 in Fig. 10b) and initial film thickness. In agreement with the electromechanical data displayed in Figs. 3-5, dielectric breakdown generally tends to increase with increasing prestrain level and copolymer concentration. The first dependence
has been explained in terms of delaying the mechanical instabilities within a given system. Since the effective rigidity of these copolymer-based DEs increases with increasing prestrain (cf. Fig. 7), the onset of pull-in instabilities, if they exist, is delayed to higher field strength so that the experimentally observed breakdown approaches the true dielectric breakdown of the material. This trend is not observed in the case of specimen films measuring 0.5 mm thick. In this case, further thinning of the DE upon prestrain most likely magnifies complications due to film defects.\[33\] Very thin prestrained films are more susceptible to catastrophic failure in the transverse direction due to single defects, whereas thick films require aligned defects (along the thickness direction) to set a failure cascade in motion. These considerations help to explain why the system with the smallest specimen thickness exhibits not only a reduction in breakdown strength with increasing prestrain but also the lowest breakdown strength of the three thicknesses examined in this figure. The apparent increase in dielectric breakdown strength with copolymer concentration, on the other hand, confirms that the intrinsic dielectric breakdown strength of the copolymer (12 - 40 kV/mm according to product literature) is higher than that of the aliphatic oil used to prepare the DE.

Another ultimate property often cited\[^{17a,33,34}\] as a performance metric is the maximum actuation strain at dielectric breakdown. For DEs able to withstand large mechanical prestrain levels prior to actuation, an equibiaxial prestrain of 300% is often employed with the intention of thinning the specimen and reducing the potential required to induce electroactuation. In Fig. 11, the prestrain is maintained constant at this level as both the initial film thickness and copolymer concentration are systematically varied. Two regimes are evident in this figure. In the first regime, the maximum actuation strain increases
monotonically (and, in some cases, almost linearly) with increasing film thickness irrespective, for the most part, of copolymer concentration. This observation is consistent with the expectation that the influence of defects decreases as the film thickness increases, thereby resulting in larger dielectric breakdown fields and associated actuation strains. Although the data exhibit scatter due to the stochastic process associated with dielectric breakdown, this regime extends up to the third specimen thickness examined here. (We recognize that the upper limit of this regime may deviate from this value, but we use this thickness to differentiate the two regimes apparent in Fig. 11.) Beyond this thickness, the maximum actuation strain can increase, decrease or remain nearly constant, depending sensitively on copolymer concentration. In this second regime, an increase in copolymer concentration promotes a reduction in the maximum actuation strain as the DE stiffness increases (cf. Fig. 7). Even after subjecting films measuring 3.0 mm thick to a 300% mechanical prestrain, the stiffer films require a large potential that causes premature failure due to surface charging and specimen heating before dielectric breakdown is reached. A similar two-regime trend has been recently observed\[16\] in other copolymer-based DEs of constant film thickness and mechanical prestrain but varying in copolymer concentration.

3.2.5. Thickness-Prestrain Coupling

Thus far, we have demonstrated that the initial film thickness (or, alternatively, the applied mechanical prestrain level) of DEs derived from SEBS/MO systems can profoundly influence the ultimate electromechanical properties at dielectric breakdown. In previous sections, the film thickness and mechanical prestrain applied prior to electroactuation have
been treated as independent quantities. In practice, however, these two parameters are coupled to yield the pre-actuation (nominal) specimen thickness, upon which the nominal electric field is calculated. Thus, the crucial analysis required to discern the importance of initial film thickness utilizes both initial film thickness and prestrain level to keep the nominal specimen thickness constant. For the maximum actuation strains presented in Fig. 12a, the initial film thickness and mechanical prestrain level are selected so that the film thickness after prestrain and prior to actuation is kept within ±5% of 0.2 mm. As in Fig. 11, two different trends are clearly discernible over copolymer concentrations ranging from 10 to 30 wt%. At low copolymer concentrations, the actuation strain increases systematically with increasing prestrain level. As the copolymer concentration is increased, however, a maximum gradually develops, indicating that a competition exists between electromechanical instability due to dielectric breakdown and instabilities induced by other mechanisms, as described by Zhang and Suo.\cite{32} Ideally, the results displayed in Fig. 12a should be largely independent of prestrain at each copolymer concentration. Since this expectation is clearly not observed, it stands to reason that the system is either behaving in highly complex fashion or the condition at which the maximum actuation is evaluated is changing even though the nominal specimen thickness does not vary. Figure 12b shows the corresponding electric field at dielectric breakdown, which, at constant nominal specimen thickness, relates directly to the applied potential. Up to 20 wt% copolymer, the breakdown field is found to increase nearly linearly with increasing prestrain. At higher concentrations, however, the line shape changes and shows evidence of saturation at 25 wt% and a maximum at 30 wt%. It is interesting to note
that the pronounced maxima in the maximum actuation strains in Fig. 12a likewise become evident at these higher copolymer concentrations (at which the systems are stiffest).

To alleviate unnecessary complications due to varying electric field (as in Fig. 12b), we have arbitrarily selected an electric field (48 V/μm) at which all the specimens possessing constant nominal thickness (after correcting the initial film thickness by the applied mechanical prestrain) display evidence of actuation. In all cases, the applied potential is the same so that the effects of initial specimen thickness and applied prestrain can be ascertained.

In Fig. 13a, the actuation strain measured under these conditions is shown as a function of mechanical prestrain for copolymer concentrations ranging from 10 to 30 wt%. A linear response is apparent at high copolymer concentrations, with deviations manifested at the low concentration end. From 20 to 30 wt% copolymer, the observed actuation strain decreases linearly (with nearly constant slopes) with increasing prestrain. According to conventional wisdom in the context of the ideal DE, however, such dependence should not exist. Clearly, the effect of mechanical prestrain on the stiffness of the elastic network seen in Fig. 7 plays an important, but largely unrecognized, role in the electroactuation of DEs. Thus, we conclude that it is insufficient to express electric fields on the basis of the nominal (prestrained) specimen thickness alone for comparative purposes. At 15 wt% copolymer in Fig. 13a, the actuation strain increases abruptly at 100% prestrain, and the corresponding strain value at 10 wt% copolymer could not be measured in the present experimental set-up. At all prestrain levels examined, this strain systematically decreases with increasing copolymer concentration (and, hence, network stiffness).
We conclude this section by introducing an additional electroactuation metric that is frequently used to assess and compare the performance of DEs: the electromechanical efficiency ($K^2$), defined as the ratio of electrical energy converted to mechanical work relative to the applied electrical energy. For elastomers capable of isochoric deformation with negligible viscous losses, $K^2$ can be expressed as

$$K^2 = 2s_z - s_z^2$$  \hspace{1cm} (11)

The functional dependence of $K^2$ on mechanical prestrain evaluated at $E = 48 \text{ V/μm}$ in Fig. 13b appears surprisingly similar to that of the actuation strain portrayed in Fig. 13a. At all the copolymer concentrations examined here, the largest electromechanical efficiencies are achieved with thin specimens equibiaxially prestrained to 100%. The value of $K^2$ systematically decreases (almost linearly) as the specimen thickness and coupled equibiaxial prestrain are increased. Although the origin of the nearly linear trends evident in Fig. 13 is not known at the present time, the consistency and well-behaved nature of these relationships at independent experimental conditions (safely removed from those responsible for material failure) is comforting and adds confidence to the ramifications of this analysis. Moreover, at a given prestrain level, $K^2$ is observed to increase with decreasing copolymer concentration and, thus, elastomer stiffness.

3.2.6. Chemically Cross-linked Systems

The coupling between initial film thickness and mechanical prestrain determined thus far for DEs composed of selectively-solvated triblock copolymer elastomers is now interrogated for two commonly used homopolymer-based DE systems. In the first case, we consider the
acrylic elastomer VHB, a commercial adhesive, which has become the benchmark standard for DEs due to its unique capability of achieving high actuation strains (in excess of 100% after 300% equibiaxial prestrain). Recent studies have demonstrated that this chemically cross-linked elastomer can also be prestrained and subsequently impregnated with a second, more rigid, network-forming species that can be polymerized in-situ to lock-in much of the original prestrain. While this clever binetwork design permits actuation strains beyond 200% without the need for further prestrain, we only consider virgin VHB further here. Two grades of VHB are available: 4905 and 4910, in which the last two digits signify the thickness (0.5 and 1.0 mm, respectively). Since we have attributed the results reported here for copolymer-based DEs to prestrain-induced changes in material properties (e.g., stiffness), we first determine whether VHB exhibits a similar dependence. Representative electromechanical stress–strain curves generated from the electroactuation responses of VHB 4905 and VHB 4910 at ambient temperature are displayed in Fig. 14a and show little difference on the basis of specimen thickness, which agrees favorably with the data provided in Fig. 9. Electromechanical moduli extracted from such curves are presented as a function of prestrain level in Fig. 14b. Included in this figure are the results of Fig. 7 recast in a comparable format. As in the case of the copolymer-based DEs, values of $Y_E$ determined for the acrylic elastomers exhibit a similarly increasing dependence on prestrain. It is also noteworthy that the moduli measured for the VHB-based DEs are larger in magnitude than any computed for the SEBS/MO systems (up to the limit of 30 wt% copolymer), indicating that VHB is an inherently stiffer material that becomes increasingly stiffer with applied prestrain.
Previous studies\textsuperscript{[17a,21,33-35]} have examined and compared the electroactuation behavior of VHB 4905 and VHB 4910 in detail, and so we do not reproduce those analyses for the two different specimen thicknesses here. Because this is a commercial material, systematic variation in specimen thickness can only be achieved by stacking layers of VHB. This practice, however, raises serious questions regarding the quality of adhesion between layers and the response of the interface separating adjacent layers to the Maxwell stress generated upon electroactuation. Because of these complications, we now turn our attention to siloxane-based DEs, which can be prepared at predetermined film thicknesses. Details regarding the synthesis of two elastomers derived from poly(dimethylsiloxane) (PDMS) with a dielectric constant of 2.65 at 100 kHz are provided in the Experimental Section. Electromechanical stress–strain curves acquired from two specimens measuring 0.2 and 0.3 mm prior to 50\% equibiaxial prestrain are displayed for completeness in Fig. 15. The low level of mechanical prestrain applied results in maximum actuation strains of 17 and 28\% at Maxwell stresses of 159 and 282 kPa, respectively. The electromechanical modulus measured from these PDMS-based DEs is 1.53 MPa, whereas the corresponding value of $Y_C$ is 0.62 MPa. Comparison of these moduli confirms that mechanical prestrain likewise increases the stiffness of this material. Although the effect of nominal specimen thickness on the electroactuation behavior of these DEs can be systematically explored, the accompanying role of mechanical prestrain regrettably cannot. These impediments associated with homopolymer-based DEs may help to explain why the effects observed during the course of the present study have not been previously reported, despite the numerous efforts devoted to the in-depth investigation of technologically viable DEs.
4. Conclusions

The objective of this work has been to elucidate the effects of initial (nominal) specimen thickness and mechanical prestrain level on the actuation behavior of large-strain dielectric elastomers. Specifically, we have examined a relatively new genre of dielectric elastomers composed of triblock copolymers swollen with a midblock-selective oil. Previous studies[15] have established that such materials, which are capable of forming elastic networks on the basis of the thermodynamics associated with microphase separation, can exhibit remarkably high actuation strains at relatively low electric fields with a high degree of electromechanical efficiency. Important considerations in the present investigation are as follows: (i) test specimens can be prepared with specific mechanical properties by systematically varying the copolymer concentration, and (ii) test specimens can be produced in different sizes and shapes to probe such process-related factors. Other material parameters, such as copolymer chemistry, composition and molecular weight, as well as solvent quality and viscosity, can likewise be controllably adjusted[36] to tailor the electromechanical properties of the resulting dielectric elastomer for a targeted analysis or application, thereby making such materials broadly tunable. Recasting conventional electroactuation data (i.e., actuation strain vs. nominal electric field) into electromechanical stress–strain curves permits determination of the electromechanical modulus in the same fashion as a purely mechanical tensile or compressive modulus. We find that this modulus (and, hence, the material stiffness) increases for both copolymer- and homopolymer-based dielectric elastomers with increasing mechanical prestrain. This observation is attributed to strain hardening of the elastic network, which tends to favor higher dielectric strength levels. The shape of the resulting stress–strain
curve is governed by the mechanical properties of the material and the level of applied prestrain. In this case, the nominal specimen thickness only affects the dielectric strength of the material. If however, a specimen is excessively thick, dielectric breakdown can be preceded by failure due to high surface currents at the compliant electrodes, accompanied by discharges and specimen heating. At a constant nominal electric field, the electromechanical properties of an ideal dielectric elastomer are not expected to vary substantially, but the results reported here are contrary to this expectation. This difference indicates that the role of material properties on the electroactuation attributes of DEs must be better understood if new, application-specific materials are to be designed for emerging responsive and energy-related technologies with efficiency and confidence.

5. Experimental

Materials: The SEBS copolymer used in this study, Kraton G1651 with a molecular weight of 265 kg/mol and a styrene content of 33 wt%, was provided by Kraton Polymers (Houston, TX). The midblock-selective solvent, a saturated aliphatic/acyclic white mineral oil (Hydrobrite 380) with a molecular weight of 503 g/mol, was obtained from Sonneborn Inc. (Tarrytown, NY). According to the manufacturer, the oil was approximately 70:30 paraffinic:naphthenic. Both components were used as-received without further purification. The chemically cross-linked acrylic homopolymers tested in this work are VHB 4905 and 4910, which were obtained from 3M Co. (Minneapolis, MN) and used as-is. The silicone elastomer was Silastic® LCF 9601, a two-component silicone product manufactured by Dow Corning Corp. (Midland, MI).
**Methods:** Measured amounts of the copolymer and oil were mixed together at 180°C for 30 min in a Ross LDM double-planetary mixer under vacuum. The block copolymer concentrations ranged from 5 to 30 wt% in 5 wt% intervals. To prevent oxidative degradation of the copolymer during mixing, 1 wt% Irganox (an antioxidant) was added. After mixing, the material was first cooled slowly to ambient temperature and then compression-molded at 180°C, followed by a rapid quench back to ambient temperature. Resultant films measured 0.5, 0.8, 1.8, or 3 mm thick. An MTS-30G instrument was used to perform quasi-static compression tests on films at ambient temperature and a constant crosshead speed of 5 mm/min. Prior to testing, a thin layer of silicone oil (which is incompatible with both SEBS and mineral oil) was applied to the top and bottom surfaces of each film to prevent the development of undesirable shear stresses during testing and thus enabling free-boundary compression testing. For electroactuation testing, a square specimen measuring 7.5 cm in length was cut from each melt-pressed film and biaxially prestrained to a predetermined level (100, 200 or 300%). Markings introduced on the film were used to discern the precise level of prestrain applied, and rigid circular frames were used to hold the prestrained films in place for electroactuation. Compliant circular electrodes, composed of silver particles suspended in a silicone matrix and obtained from Chemtronics Circuit Works (Kennesaw, GA), were applied to both sides of each film. Edge effects were avoided by keeping the active area of the electrodes small (~1-2%) relative to the total film area. Leads painted on each side were connected to a Bertan 225-30R high-voltage power supply (Spellman High Voltage Electronics Corp., Hauppauge, NY) controlled by a Labview program that synchronized the
power supply with a video camera designed to collect continuous images of actuating specimens as a function of time. The applied voltage was fixed at a rate of 250 V/s and was varied from zero to film breakdown. Acquired images were analyzed using image analysis software, and the actuation strain was calculated according to Section 2. The dielectric constant of several unstrained specimens was measured at ambient conditions with a dielectric test fixture (Agilent 16451B) connected to a HP4284A LCR meter operated over a frequency range of 20 Hz to 1 MHz. Silicone films were produced by mixing the elastomer base and catalyst of the Silastic® LCF 9601 system at a 95:5 weight ratio in a Mazerustar KK-400W planetary mixer. Hexane was added prior to mixing to reduce the mixture viscosity. After mixing, the solution was cast into Teflon trays for 24 h to permit complete evaporation of hexane. Resultant films were annealed under vacuum at 160 °C for 15 min to promote complete curing of the system.

6. Acknowledgments

This work was supported by the National Science Foundation and Eaton Corporation.
Figure 1 Schematic diagram depicting the test configuration and electroactuation mechanism of dielectric elastomers, as well as the coordinate system used in the text.
Figure 2 In (a), compressive stress ($\sigma_C$) presented as a function of transverse (thickness) strain ($-s_z$) for a SEBS/MO elastomer with 30 wt% copolymer (○). Included are corresponding stress values predicted by fitting the Ogden model to uniaxial tensile data acquired from the same material, followed by the transformations described in the text (●). In (b), compressive moduli ($Y_C$) extracted from data such as those in (a) and displayed as a function copolymer concentration. The solid lines denote power-law fits to the data.
Figure 3 Area actuation of SEBS/MO dielectric elastomers equibiaxially prestrained to 100% from initial specimen thicknesses of (a) 0.5, (b) 1.0 and (c) 1.8 mm for different copolymer
concentrations (in wt%): 10 (⊙), 15 (●), 20 (△), 25 (▲) and 30 (◇). The solid lines serve as guides for the eye.
Figure 4 Area actuation of SEBS/MO dielectric elastomers equibiaxially prestrained to 200% from initial specimen thicknesses of (a) 0.5, (b) 1.0 and (c) 1.8 mm for different copolymer
concentrations (in wt%): 5 (♦), 10 (○), 15 (●), 20 (△), 25 (▲) and 30 (◇). The solid lines serve as guides for the eye.

Figure 5 Area actuation of SEBS/MO dielectric elastomers equibiaxially prestrained to 300% from initial specimen thicknesses of (a) 0.5, (b) 1.0, (c) 1.8 and (d) 3.0 mm for different copolymer concentrations (in wt%): 5 (♦), 10 (○), 15 (●), 20 (△), 25 (▲) and 30 (◇). The solid lines serve as guides for the eye.
Figure 6 Electromechanical stress–strain (Maxwell stress–transverse strain) curves derived for SEBS/MO dielectric elastomers with an initial specimen thickness of 1.8 mm and equibiaxially prestrained to (a) 100, (b) 200 and (c) 300% for different copolymer
concentrations (in wt\%): 5 (●), 10 (○), 15 (●), 20 (△), 25 (▲) and 30 (◇). The solid lines are guides for the eye.

Figure 7 (Electro)mechanical moduli of SEBS/MO dielectric elastomers presented as a function of copolymer concentration. Purely compressive moduli ($Y_c$) are displayed as (●), whereas electromechanical moduli ($Y_E$) are acquired from specimens at different prestrain levels (in %): 100 (○), 200 (▲) and 300 (△). The solid lines denote power-law fits to the data.
Figure 8 Master curve obtained after normalizing the Maxwell stress by the
electromechanical modulus for all the SEBS/MO systems shown in Figs. 6a-c. For
consistency, the same symbols are used, and the solid line serves as a guide for the eye.
Figure 9 Electromechanical stress–strain curves for SEBS/MO dielectric elastomers with 25 wt% copolymer and equibiaxially prestrained to (a) 100, (b) 200 and (c) 300% for different
initial specimen thicknesses (in mm): 0.5 (●), 1.0 (○), 1.8 (▲), and 3.0 (△). The solid lines serve as guides for the eye.
Figure 10 Dielectric strength of SEBS/MO dielectric elastomers with (a) 10 and (b) 30 wt% displayed as a function of equibiaxial prestrain for specimens varying in initial thicknesses (in mm): 0.5 (●), 1.0 (○), 1.8 (▲), and 3.0 (△). The solid lines connect the data.
Figure 11 Maximum area actuation evaluated at dielectric breakdown for SEBS/MO dielectric elastomers equibiaxially prestrained to 300% and varying in copolymer concentration (in wt%): 5 (♦), 10 (○), 15 (●), 20 (△), 25 (▲) and 30 (◇). The solid and dashed lines connect the data.
Figure 12 In (a), maximum area actuation at dielectric breakdown for SEBS/MO dielectric elastomers varying in initial thickness so that, upon equibiaxial prestrain, the pre-actuation specimen thicknesses remain constant at 0.2 mm (± 5%). In (b), the corresponding breakdown electric fields are displayed. The copolymer concentrations are designated (in wt%) as 10 (○), 15 (●), 20 (△), 25 (▲) and 30 (▽). The solid lines serve to connect the data.
Figure 13 Electroactuation performance metrics evaluated at a true electric field of 48 V/μm for SEBS/MO dielectric elastomers with a constant thickness after prestrain of 0.2 mm at 0 V. In (a) and (b), the area actuation and electromechanical coupling efficiency are displayed as functions of equibiaxial prestrain at different copolymer concentrations (in wt%): 10 (O), 15 (●), 20 (∆), 25 (▲) and 30 (◇). The solid lines serve to connect the data.
Figure 14 In (a), electromechanical stress–strain curves for VHB 4905 (open symbols) and 4910 (filled symbols) equibiaxially prestrained to different levels (in %): 100 (circles), 200 (triangles) and 300 (squares). In (b), electromechanical moduli of DEs derived from both SEBS/MO systems (copolymer concentrations, in wt%, are labeled) and VHB (4905, ▲; 4910, ○) displayed as a function of equibiaxial prestrain. The solid lines serve as guides for the eye in (a) and connect the data in (b).
Figure 15 Electromechanical stress–strain curves for silicone elastomers equibiaxially prestrained to 50% and varying in initial thickness (in mm): 0.2 (□) and 0.3 (■).
7. References


