ABSTRACT


Thermoplastic elastomers are a class of rubbery polymeric materials that exhibit solid-like properties due to physically associating moieties. Block copolymers are often used as the network forming component of thermoplastic elastomers. Additionally, block copolymers can be modified with block selective solvents that contribute a specific functionality to the system; these solvent modified systems will be referred to throughout as thermoplastic elastomer gels. Thermoplastic elastomers and their gels have a long history of applications as specialty materials for passive systems where traditional rubbers cannot meet the required design criteria—often properties of softness, toughness and low hysteresis are of interest. Herein, we discuss the use of thermoplastic elastomer gels as active materials that respond to external stimuli to change their mechanical and thermal properties.

First, the text will introduce concepts of phase behavior and resultant physical behavior of block copolymers in the presence of a selective solvent. Included are specific details pertinent to materials used in experimental discussions presented in this work. Following this broad discussion, the introduction of a specific class of smart and responsive materials, known as dielectric elastomer actuators, is detailed in a survey of recent technological developments in the field.

The main body of the text describes multiple applications of thermoplastic elastomer gels. It begins with an entirely novel use of a semi-crystalline olefin block polymer gel as a dielectric elastomer actuator exhibiting programmable anisotropy and promising actuation behavior. The subsequent study uses specific control over the architecture of a
polydimethylsiloxane elastomer to make ultra-soft films for exceptional dielectric elastomers. These so-called bottlebrush elastomers are formed from heavily grafted polymer backbones that reduce entanglements resulting in incredibly soft elastomers. As dielectric elastomers, these materials operate with no mechanical prestrain and achieve strains greater than 300% by area. This is followed by the use of a traditional ABA triblock copolymer (poly[styrene-\textit{b}-ethylene-\textit{co}-butylene-\textit{b}-styrene]) with a crystallizing selective solvent to impart shape memory behavior. This is the first demonstration of a dielectric elastomer utilizing crystallization for electroactive strain fixation. Finally, we conclude with the discussion of thermoplastic copolyester based gels as form-stable phase change materials. These phase change gels have applications in passive thermal energy management systems and compete with existing commercial technologies.
Responsive Thermoplastic Elastomer Gels: Applications in Electroactive, Shape-Memory and Thermal Energy Management Materials

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 Doctorate of Philosophy

Chemical Engineering

Raleigh, North Carolina

2017

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DEDICATION

This dissertation is dedicated to my family. To my wife, Jenna, who has been with me as a force of encouragement, stability and inspiration, and who convinces me to enjoy life when I take it too seriously. To my parents and my brother, Hampton, Mechelle and Michael, who provided me with a nurturing environment and unconditional support throughout my life; they have given me all of the opportunity in the world to be the best version of myself. And to my new son who is giving me the motivation to persevere until the end.
BIOGRAPHY

I was born in Huntsville, Alabama in the Southeastern United States of America, the first-born child of Mechelle and Hampton Armstrong. I graduated from Bob Jones High School in 2007 and continued my education at the University of Alabama in Tuscaloosa, Alabama on a partial athletic/partial academic scholarship. At Alabama I was a multi-time conference scorer, a U.S. Nationals qualifier and U.S. Olympic Trials qualifier in 2012. I graduated from Alabama in 2011 with a major in Chemical and Biological Engineering and a minor in Chemistry. I worked for a short time as an assistant research chemist at Avanti Polar Lipids in Alabaster, Alabama before accepting a research assistantship position at North Carolina State University. In July of 2012, I was married to my partner, Jenna Montgomery Armstrong. Jenna and I met while swimming for the University of Alabama. We moved to Raleigh soon after our wedding to begin our respective doctoral studies. I took a short break during my doctoral research to intern at Lord Corporation in Cary, North Carolina in their New Business Development and Chemical Sourcing groups.
ACKNOWLEDGMENTS

Thanks are in order to many people for assistance with the work in this dissertation. First and foremost, thanks to the Macromolecular Materials and Morphology Group for your assistance both personal and professional. Specifically, thanks to Kenny Mineart, Justin Ryan, Mohammad Tuhin, Jacob Majikes and Heba Al-Mohsin who all had direct impacts on this work through conversation and collaboration. Additionally, a thanks to every undergraduate student who contributed to this work, specifically Steve Lim, Madeline Poole, Firass Amra, Joshua Dickerson, Caitlyn Joyner, Jessica Manning, Gabe Chauvigne, Kaleb Morrow, Zach Ledford and Chris Cooper.

A major thanks to my committee members, Dr. Michael Dickey, Dr. Saad Khan, Dr. Tushar Ghosh and their research groups for resources, both physical and intellectual. Without some informative conversations and a generous sharing of laboratory resources, this work would not have been possible. A special thanks to the Dickey research group for their especially gracious assistance in providing me lab space and resources as if I was “one of their own”.

Thanks to Dr. Sergei Sheiko’s group at UNC for collaborating on the Bottlebrush Dielectric Elastomer project. I was very grateful to be included on such a groundbreaking paper. Also, thanks to all the staff in the Chemical Engineering Department who keep the department running smoothly.

And finally, thanks to Dr. Richard Spontak for your patience and support while guiding me through this long process, and to Dr. Michael Dickey for your pro bono time and effort spent in guiding my work.
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$(\lambda_a - 1) 100\% = 300 \pm 50\%$ and $25 \pm 5\%$, respectively. Both samples employ the same PDMS bottlebrush elastomer ($n_{sc} = 14, n_g = 1, n_x = 200$).

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**Figure 6.1.** The proposed process of bimorphic shape memory using a dielectric elastomer film. Blue indicates temperatures below the hydrocarbon melting point and red indicates temperatures above the melting point. Black arrows designation a change in electrical charge state (*i.e.* DC biasing). In state (A), a dielectric elastomer film with compliant electrodes exists in a state of no applied voltage ($V = 0$) and a temperature below the melting point ($T < T_m$). The inset shows a block copolymer network wherein the elastic chains are immobilized by a network of paraffin crystallites. In state (B), a high frequency electric field is applied across the DEA ($\Omega \sim 10 \ \text{kHz}$, above the resonant mechanical frequency). Energy is dissipated by mechanical loss, dielectric loss and joule heating to heat the DEA to a temperature $T > T_m$. The inset of (B) shows the thermoplastic elastomer network in a midblock selective liquid solvent that exhibits the behavior of a thermoplastic elastomer gel. In state (C), the high frequency signal is rectified to a high voltage DC signal and the DEA actuates by a reduction in thickness.
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**Figure S6.2.** Simple predictions for melt time of a 1mm thickness bimorph DEA based on the dielectric heating contribution without heat losses.

**Figure S6.3.** Shear rheological measurements of S/C/T films to study the effects of crystallization on mechanics. A) Changes in shear modulus of S/C/T films over time are given as a ratio of the initial modulus of the gel \((G'_0 = G' \text{ at } 50^\circ\text{C where } T > T_{\text{melt}})\). Different conditions are shown by each data set: red circles (○) are S/C/T:30/50/20 crystallized at 35°C, light blue circles (○) are S/C/T:30/50/20 crystallized at a cooling rate of 5°C/min, dark blue circles (○) are S/C/T:30/50/20 crystallized at 2°C/min, and black triangles (▲) are S/C/T:20/80/00 crystallized at 2°C/min. The plateau modulus is much higher with high concentrations of paraffin due to the highly percolated network of paraffin crystals. The plateau modulus of S/C/T:20/80/00 is approximately \(4 \times 10^7\) and the plateau modulus of S/C/T:30/50/20 is \(\sim 1 \times 10^6\). B) Temperature sweep of S/C/T:20/80/00.

**Figure S6.4.** Strain fixity of S/C/T:30/50/20 in tensile extension. Set strain is 300%. Fit with a first order exponential of the form 

\[ f_t = f_\infty (1 - e^{-k(t-t_{lag})}) \]

where \(k\) is a crystallization rate constant, \(t_{lag}\) is a constant associated with crystal nucleation, and \(f_t\) is the strain fixity as a
function of time. The strain fixity as $t \to \infty$, $f_\infty$, is calculated to be 95%. This corresponds well with electroactuation results of S/C/T:30/50/20.

**Figure 7.1.** A) Crystallization and melting enthalpies of oleic acid following thermal exposure. A first order exponential fit is used as a model assuming a first order oxidation reaction, but is not meant to be mechanistically representative. B) Discoloration of oleic acid (Pamolyn 100) after thermal exposure in oxygenated atmosphere at 195°C.

**Figure 7.2.** Results of a solvent exusion test conducted on a hydraulic press. Solid mass fractions are measured after successive application of pressure. Pressures are given in metric tons/16 in$^2$. The black curve represents total remaining mass fraction on a gel basis and the blue curve represents remaining mass of fatty acid based on the initial fatty acid mass within the form stable gel.

**Figure 7.3.** Quasi-static tensile extension tests of TcPE 9965 with no fatty acid additive ($\bullet$) compared to 9965-O-25. The tensile modulus changes from 106.8 MPa to 9.33 MPa with the addition of fatty acid (Pamolyn 100). The inset shows the drastic decrease in strength and toughness upon the addition of fatty acid that swells short amorphous chains.

**Figure 7.4.** A) Melting temperatures of TcPE-9965 with oleic acid (Pamolyn 100) over a range of compositions. Dotted lines indicate the average melting temperatures over the entire range of compositions as there is no significant deviation in melting temperature. B) Melting
temperatures of TcPE-9965 with linoleic acid (Pamolyn 200). There appears to be a slight dependence of melting and crystallization point on composition.

**Figure 7.5.** A) Melting and Crystallization of TcPE9965-OA-60 showing 6 consecutive heating and cooling cycles. A point of note is the disrupted melting peak of the linoleic acid rich phase which consistently. B) A single DSC trace of OA showing two distinct melting peaks for an oleic acid rich phase at ~0°C and a linoleic acid rich phase at ~-20°C. C) DSC curves of LA and 50 weight percent mixtures of TcPE and LA with grades labeled on the plot. Heat flow is given in arbitrary units.

**Figure 7.6.** A) Enthalpy of Crystallization of TcPE 9965 as a function of composition considering only the primary peak (i.e. over a temperature range of ~0 to 20°C. Crystallization integrations are shown in blue and melting integrations shown in red. B) Comparison of the enthalpy of fusion (melting) of 9965 (●), 9966 (●) and 9967 (●) TcPEs as a function of oleic acid fraction considering all enthalpic melting peaks over a range of approximately -20 to 20°C.

**Figure 7.7.** Traces from DSC of TcPE 9967 gels of varying mass fraction label on the plot. The secondary peak (linoleic acid rich phase) gradually spreads out over a large temperature range.

**Figure 7.8.** A) Comparison of TcPE based form-stable PCM to a commercial microencapsulated product. B) The suggested loading for applications of microencapsulated
paraffin PCM are ~40% by volume, whereas the TcPE form-stable PCM can be used at a 70% loading. This comparison gives a more realistic enthalpy of fusion for PCMs used for energy management or energy storage applications.

**Figure 8.1.** (A) Material models of a composite dielectric material (PMN-PT particles in SEBS) are used to predict static dielectric constant (●) using the Maxwell-Wagner model and shear modulus$^{33}$ (●), $G'$. (B) The normalized transverse strain coefficient ($\varepsilon_0\varepsilon'/G'$) is given as a function of filler volume fraction. It is evident that even in the best case of stiff fillers with a very large dielectric constant, such as PMN-PT, modest gains can be made in DE actuator improvement and those improvements come at the cost of decreased dielectric breakdown strength.

**Figure 8.2.** The Maxwell-Wagner composite model is used to predict the dielectric constant of TPEGs using SnBAS triblock copolymers and two carbonate solvents. The midblock is assumed to be miscible with the solvents and the endblocks completely immiscible.

**Figure 8.3.** (A) Model of proposed block copolymer architecture where blue beads represent polystyrene and red beads represent a polar repeat unit, specifically n-butyl acrylate, methacrylate, methyl methacrylate, ethylene oxide or acrylonitrile. The location of styrene chains is random, but the “graft” density is tunable through relative polymerization concentrations of polar monomer and polystyrene macromonomer. (B) Proposed synthesis of functionalized polystyrene macromonomer.
**Figure 8.4.** (A) Layered Hydrogel composite schematic with compliant electrodes applied to either side of a tri-layer composite: SEBS/MO-Aam/Glycerol-SEBS/MO. The SEBS/MO passivating layer is 15% polymer by weight. (B) Image of layered composite amphigel DE. (C) Transverse actuation strain of an amphigel layered composite elastomer to breakdown voltage.

**Figure 8.5.** (A) Areal actuation strain of biaxially prestrained SEBS elastomer and a SEBS/Aam composite. (B) Electromechanical anisotropy of fiber enforced SEBS/Aam composites.

**Figure 8.6.** The miscibility of ternary mixtures of SEBS-OSP-MO gels are shown.

**Figure 8.7.** The dielectric constant of three SEBS-based TPEGs are measured over a broad range of frequencies, (●) SEBS-OSP-MO (20/20/60 weight %, respectively) and (●) SEBS-MO (20/80 weight % respectively).

**Figure 8.8.** Electroactuation tests of ternary component gels (SEBS-OSP-MO) of varying copolymer and MO composition (OSP fixed at 20 weight percent). Addition of OSP decreases poling voltage when compared to SEBS-MO DEs, but also appears to decrease the dielectric breakdown strength—explaining the failure at low strain.

**Figure A.1.** Schematic illustration of the QS-DSSC fabricated with a sulfonated block ionomer (SBI) as the polymer gel electrolyte. The TEM images in (a) and (b) display the
SBI2.0 morphologies (with the ionic regions selectively stained to appear dark) generated by solvent casting from THF and TIPA, respectively.

**Figure A.2** SAXS profiles acquired at ambient temperature from TIPA-cast (black) and THF-cast (green) SBI2.0 before (dry) and after incorporation of the HI-30 iodolyte (labeled). The filled arrowheads identify the principal scattering peak, $q^*$, in each profile, whereas the open arrowheads mark higher order scattering peaks (ratios to $q^*$ labeled).

**Figure A.3** In (a), cryofractured cross-sectional SEM image of a QS-DSSC containing the THF-cast SBI2.0 imbibed with HI-30 iodolyte. The averaged elemental traces for titanium, carbon and iodine track the spatial distribution of TiO$_2$, SBI and iodolyte, respectively, across the SBI/TiO$_2$ heterojunction. While the dashed blue lines on the SEM images identify the apparent interface, the solid/dashed lines indicate a broader interface on the basis of elemental composition. The SEM image in (b) displays the diffuse surface of the TiO$_2$ layer prior to SBI deposition.

**Figure A.4** Photocurrent density presented as a function of voltage under the conditions specified in the text (a) and incident photon conversion efficiency (IPCE) shown as a function of wavelength (b) for QS-DSSCs containing THF-cast SBI grades differing in midblock IEC: 1.0 ($\Delta$), 1.5 (●) and 2.0 (○). The solid lines serve to connect the data.

**Figure A.5** Voltage dependence of the photocurrent density for QS-DSSCs containing (a) THF- and (b) TIPA-cast SBI2.0 with the three different photosensitizers depicted in [Scheme](#).
A.1: NCSU10 (△), HD15 (●) and N719 (○). The solid lines serve to connect the data.

Figure A.6 Wavelength dependence of the IPCE for QS-DSSCs containing THF- (○) and TIPA-cast (●) SBI2.0 with the photosensitizers (a) N719 and (b) HD15. The solid lines serve to connect the data.
An elastomer is a polymeric material that exhibits some of the properties of a solid and some of the properties of a liquid—commonly referred to as a viscoelastic material. Elastomers are comprised of liquid polymer chains, i.e. polymers with a glass transition ($T_g$) below room temperature, that have inter-chain linkages which are fixed. These fixed linkages are called crosslinks, and they give the macromolecular structure a permanent shape and contribute significantly to the viscoelastic behavior of the polymer. Generally, high numbers of crosslinks contribute to higher strength, stiffness and brittleness while a low degree of crosslinking results in soft materials with high extensibility.

The vast majority of elastomers in commercial use are chemically crosslinked, or thermoset, materials. A smaller subset of elastomeric materials take advantage of physically associating moieties to form physical crosslinks meaning the forces associated with transferring energy throughout the network of polymer chains are intermolecular in nature. These physical associations can be either enthalpic or entropic in nature, but are considered to be reversible through some stimulus, e.g. a thermal transition temperature or exposure to a solvent. One of the most common examples of thermoplastic elastomers is block copolymers, which will be the focus of this discussion and the work that follows in this dissertation.

Block copolymers are defined as two or more polymers with unique repeat unit chemistries that are covalently linked together. A linear diblock copolymer is the simplest architecture of block copolymers consisting of a chain of polymeric repeat units of chemical identity ‘A’ that are covalently linked to a chain of repeat unit ‘B’. Many more architectures
are possible including highly complex architectures; prominent examples of block copolymers that are featured in the following work include linear ABA triblock copolymers, graft block copolymers and multiblock copolymers (Figure 1.1). To create effective thermoplastic elastomers from block copolymers, two conditions must be met. First, at least one of the blocks must be repeated within the copolymer chain. For example, a common architecture for a thermoplastic elastomer is an ABA triblock copolymer. Blocks must repeat within a single chain so that linkages can be formed by physically associating chains to form networks. These linkages are referred to as “bridges”, and they connect spatially separated anchor points that comprise the physical crosslinks. Secondly, physically associating blocks must be mechanically stable, meaning that physically associating linkages are either glassy liquids or crystalline solid domains at the operating temperature. For elastomeric behavior, the bridges must also be liquid polymer chains above their glass transition temperature.

Block copolymers with these specific architectural characteristics behave as thermoplastic elastomers due their inherent propensity to phase segregate. Because of the covalent linkages present in block copolymers, this phase segregation must take place on small length scales, on the order of the radius of gyration of the polymer chain,\(^1\) rather than the macroscopic scale phase segregation of small molecules. For this reason, we deem phase segregation of block copolymers as microphase separation and the resulting size scales are typically on the order of 10s of nanometers. This self-organization can occur in a variety of morphological structures; common structures of microphase separated block copolymers include alternating lamellae, hexagonally packed cylinders and spheres in a continuous matrix. These structures are shown in Figure 1.2.\(^2\) Minimization of free energy in block copolymer
systems requires a minimization in surface energies leading to the formation of microphase separated domains. As a result, the morphology is determined by the relative fractions of each polymer species, $f_i$, the incompatibility of each species measured by the Flory-Huggins interaction parameter, $\chi$, and the degree of polymerization, $N$.

### 1.1 Thermoplastic Elastomer Gels – Block Copolymers with Selective Solvents

The main body of this work focuses on thermoplastic elastomers with an additional solvent added that is selective to the soft block(s) of the polymers. Particularly, it examines thermoplastic elastomer gels (TPEGs) that contain a low volatility solvent that provides functionality to the overall gel. Physical crosslinks must remain rigid for mechanical integrity of the network, and thus solvents must be selective to the soft, rubbery blocks so as not to plasticize and dissolve physical crosslinks. The same morphological structures found for block copolymers can be preserved in TPEGs, and therefore the elastomeric behavior is preserved in gels with a high polymer concentration.

To make functional TPEGs, the properties that influence solubility and the formation of polymer solutions must be understood. The miscibility of a given polymer and solvent combination is governed by a free energy expression

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

Eqn. 1.1

wherein mixing is energetically favorable when $\Delta G_{mix}$ is negative. In some cases, strong intermolecular interactions such as dipole-dipole, ionic or hydrogen bonding can provide sufficiently favorable enthalpic energy to promote miscibility of two unlike chemical species. Mixing of non-polar species have a net positive enthalpy. Enthalpic interactions can be
accounted for by the Flory-Huggins interaction parameter which is a function of temperature and commonly empirically defined as

$$\chi = a + \frac{b}{T} \quad \text{Eqn. 1.2.}$$

where $a$ and $b$ are pairwise constants. The free energy of mixing of a homopolymer in solution can then be reduced to specific terms of

$$\Delta G_{mix} = RT(n_1 \ln(\phi_1) + n_2 \ln(\phi_2) + n_1 \phi_2 \chi) \quad \text{Eqn. 1.3.}$$

It should be obvious at this point, that the value of $\chi$ is critically important in understanding the phase behavior of block copolymers and TPEGs. We therefore need reliable correlations to predict the value of $\chi$ when designing TPEG systems. Determination of $\chi$ from easily obtainable physical properties can be done by relating $\chi$ to a solubility parameter, $\delta$. The solubility parameter, as originally described by Hildebrand,$^3$ is a function of the cohesive energy density of a liquid, i.e. the heat of vaporization, $\Delta H_v$ by

$$\delta = \left[\frac{\Delta H_v - RT}{V}\right]^{1/2} \quad \text{Eqn. 1.4.}$$

As polymers don’t have a measurable vapor pressure, solubility parameters must be determined by implicit relation to solvents with known solubility parameters. Additionally, group contribution methods have been developed$^4$ that can be used to estimate solubility parameters of polymers. The Flory-Huggins interaction parameter is related directly to the solubility parameter according to the relationship

$$\chi_H = \frac{V(\delta_1 - \delta_2)^2}{RT} \quad \text{Eqn. 1.5.}$$

When the solubility of two polymers is being considered, the entropic contribution to the $\chi$ parameter is small and considered negligible such that $\chi = \chi_H$. When small molecule solvents
are included, an entropic term must be considered, and $\chi_s$ has a value of 0.2-0.3 resulting in $\chi = \chi_H + \chi_s$. For molecules with intermolecular interactions more complex than dispersion forces, hydrogen bonding and polar interactions must be considered in separately. Hansen has described these interactions in detail by breaking up the overall solubility parameter into separate contributions such that

$$\delta = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{1/2}$$  \hspace{1cm} \text{Eqn. 1.6.}

Addition of solvent to a polymer network has a substantial effect on the mechanical properties of the system. A polymer gel is defined as a network of crosslinked chains with a network that spans the entirety of the collective material. The mechanics of gels are often probed with rheological measurements. Dynamic rheological measurements can sensitively provide information about the relative liquid and solid like behavior of a polymer solvent system. The ratio of mechanical loss modulus to storage modulus defines the value

$$\tan(\delta) = G''(\omega)/G'(\omega)$$  \hspace{1cm} \text{Eqn. 1.7.}

It has been thoroughly demonstrated that the critical gel composition (i.e. the lower limit of network formation) occurs when the value of $\tan(\delta)$ is frequency independent. The Winter-Chambon criterion holds for thermoplastic elastomer gel systems, though it must be considered on a temperature and composition basis as opposed to a time-dependent basis.

Addition of solvent also drastically modifies the mechanical response of thermoplastic elastomers. A selective solvent will lubricate bridging chains in a thermoplastic elastomer gel network and can reduce entanglements in solvent swollen polymer chains. This results in the possibility of tailoring the mechanical modulus of a TPEG over multiple orders of magnitude by simply changing composition with simple mix and stir processes.
The fundamental principles of block copolymers, polymer solubility and gel mechanics are described above to be used as basic tools and a starting point for designing thermoplastic elastomer systems. This short review only just touches on the literature of thermoplastic elastomer gels to provide a conceptual basis. The following discussion will be a brief overview of the literature in application areas relevant to the research presented in subsequent chapters. Electroactive materials are covered in detail in the following chapter, so here we will focus on two materials that take advantage of phase transitions in their function, shape memory polymers and phase change materials.

1.2 Shape Memory Polymers

Shape memory materials have generated interest as smart materials capable of responding to thermal, optical and other external stimuli. The scope of this overview will be limited to thermally responsive shape memory polymers that change shape and rigidity upon crossing a thermal transition, \( T_{\text{trans}} \). The change in mechanical response of a shape memory polymer is due to a first order or second order liquid-solid phase transition, i.e. a crystallization or glass transition. Shape memory polymers are designed on the principle that multiple networks are formed. The first network is deemed permanent, or at least semi-permanent, and the secondary network is formed and disassembled as a result of the traversing the transition temperature.

For thermally responsive shape memory polymers, elastomeric behavior is present above \( T_{\text{trans}} \), and solid behavior is typical below \( T_{\text{trans}} \). This double network can be created through a variety of means. Elastomers with crystallizable soft segments,\textsuperscript{14} elastomer gels with crystallizable solvents,\textsuperscript{15} and thermoplastic elastomers containing a soft block with a phase
transition. The process of cycling a shape memory polymer is depicted in Figure 1.3, reproduced from Lendlein et al. In this fashion, shape memory polymers can be “programmed” with a new shape different than the shape of the permanent network. Upon reversal of the stimulus, a perfect shape memory material will return to its permanent shape.

Important performance metrics to gauge the performance of shape memory materials that require cyclic use are the strain fixity and strain recovery. Strain fixity, $f_e$, defines the ability of a shape memory polymer to hold a programmed shape as

$$f_e = \frac{\varepsilon_u}{\varepsilon_m} \tag{Eqn. 1.8}$$

and strain recovery, $r_e$, is defined as

$$r_e = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \tag{Eqn 1.9}$$

Work involving this class of materials is discussed in Chapter 6.

1.3 Phase Change Materials

In addition to changing the mechanics of an elastomeric system, first order phase transitions also require a sizeable latent heat contribution without a change in temperature. In phase change materials, the first order phase transition is coopted for the purpose of thermal energy storage and temperature management. These materials have potential for applications in improved insulation, passive and energy saving climate control, and even energy storage in renewable energy capture technologies.

Phase change materials are primarily small molecules with high latent heat. Phase change materials are often categorized as organic and inorganic materials. Common inorganic materials are various salt hydrates, while common organic phase change materials include
paraffins, fatty acids and aromatics. Inorganics tend towards higher latent heats and higher transition temperatures (>100°C) while the inverse is true for organics. Polymers and oligomers have been used as phase change materials as well, but high molecular weight polymers suffer from incomplete crystallization, lowering the overall enthalpy of fusion per unit volume.

High molecular weight polymers do have the advantage of viscoelastic behavior above their transition temperature, while small molecule phase change materials are low viscosity liquids. Low viscosity liquids flow readily and require some form on containment. Containment can be done on a macroscopic scale for simplicity or on a microscopic scale to improve heat transfer and mitigate the effects of volume change. A solution for freestanding phase change materials is the use of polymer networks to construct “form stable” phase change materials. These are polymer gels that contain a phase change material as a solvent. Many variations of this have been demonstrated, including paraffin/HDPE gels, and paraffin impregnated particle board. Further discussion of a novel form stable phase change material is presented in Chapter 7.
**Figure 1.1.** From left to right, cartoon depictions of block copolymers: ABA triblock copolymer, AB graft copolymer and AB multiblock copolymer. Depending on the polymerization method, block lengths, block polydispersity, number of blocks and block purity are all variables.
Figure 1.2. Reproduced from Matsen and Bates.\textsuperscript{2} Phase diagram of a diblock copolymer with the classical morphologies depicted below.
Figure 1.3. Description of the shape memory behavior of a polymer under one cycle of strain, strain fixing and recovery. (1) A shape memory polymer above $T_{\text{trans}}$ is stretched to a maximum applied strain, $\varepsilon_m$. (2) Temperature is dropped below $T_{\text{trans}}$. (3) External stress is removed and strain relaxes to a set strain, $\varepsilon_u$. (4) Temperature is raised above $T_{\text{trans}}$ and the elastomer relaxes back to a recovered strain, $\varepsilon_p$. (5) A second cycle is initiated by stretching the elastomer back to $\varepsilon_m$. Figure reproduced from Lendlein et al.\textsuperscript{17}
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Designing Dielectric Elastomers over Multiple Length Scales for 21st-Century Soft Materials Technologies

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Dielectric elastomers (DEs) constitute an increasingly important category of electroactive polymers, a class of generally soft materials that, upon exposure to an electric stimulus, respond by changing size and/or shape. Derived from network-forming macromolecules, DEs are lightweight, robust and scalable, and they are furthermore capable of exhibiting giant electroactuation strains, high electromechanical efficiencies and relatively low strain-cycling hysteresis over a broad range of electric fields. Due primarily to their attractive electromechanical attributes, DEs are of growing interest in diverse biomedical, (micro)robotic, and analytical technologies. Since the seminal studies of these electroresponsive materials (initially fabricated mainly from chemically-crosslinked acrylic and silicone elastomers), advances in materials design over multiple length scales have resulted in not only improved electromechanical performance but also better mechanistic understanding. In this work, we first review the fundamental operating principles of DEs developed for conventional elastomers that undergo isotropic electroactuation and then consider more recent developments at different length scales. At the macroscale, incorporation

†his review has been published in Rubber Chem. Tech. (citation)
of oriented fibers within elastomeric matrices is found to have a profound impact on electroactuation by promoting an anisotropic response. At the mesoscale, physically-crosslinked thermoplastic elastomer gel networks formed by midblock-swollen triblock copolymers provide a highly tunable alternative to chemically-crosslinked elastomers. At the nanoscale, the chemical synthesis of binetwork and bottlebrush elastomers permits extraordinarily enhanced electromechanical performance through targeted integration of inherently prestrained macromolecular networks.

I. INTRODUCTION

In response to a growing need for smart, or intelligent, materials over a wide range of mature and emerging technologies, stimuli-responsive polymers have earned a significant niche due to their intrinsic chemical versatility, facile processability, low cost, light weight, and mechanical durability.\textsuperscript{1-5} While macromolecules capable of responding to external stimuli such as changes in temperature, light or pH have been extensively studied, electroactive polymers (EAPs) constitute a broad class of macromolecular-based materials that systematically respond to an electric stimulus by changing size and/or shape upon exposure.\textsuperscript{6-10} These materials are further categorized according to the mechanism by which they undergo electroactuation. An ionic EAP membrane, for example, requires the presence of a polar liquid for solvated ions to migrate across the membrane and, in so doing, induce an electro-osmotic pressure gradient as the membrane undergoes non-uniform swelling.\textsuperscript{11-13} The commonly encountered outcome of such electroactuation observed, for instance, in ionic polymer-metal composites (IPMCs) is a bending motion that, upon rapid cycling, can be used to mimic aquatic (fish-style) locomotion.\textsuperscript{14,15} Other examples of ionic EAPs include carbon nanotube forests.\textsuperscript{16,17}
Because electrons flow in electronic EAPs as they respond to an applied electric field, a liquid medium is not necessary. Examples of electronic EAPs include ferroelectrics such as poly(vinylidene fluoride) (PVDF) and its copolymers, which electroactuate as a consequence of a field-induced phase transition, and dielectric elastomers (DEs). Due to the giant actuation strains, high electromechanical efficiencies and low strain-cycle hysteresis achieved with this family of EAPs, only DEs are considered further in this work, and details of their operating principle are provided in Section II.

Devices fabricated from DEs are increasingly garnering attention because of the nontrivial benefits they afford over more established transducers for actuator and generator technologies. For cyclic and high-strain applications, the mechanical compliance and toughness of DEs are vastly superior to more mature electromechanical transducer technologies based on, for example, electroactive ceramics, which achieve relatively small electroactuation strains and often fail due to their inherent brittleness. Scalability represents another growing design consideration, since actuators that employ traditional (e.g., pneumatically-driven) motors lose their efficiency when scaled down to dimensions often encountered in biomedical and microrobotic technologies. For reasons such as this, candidate materials capable of advancing soft robotics are highly sought to replace inefficient or cumbersome mechanical actuators, especially as anthropomorphic machines constructed from DEs are envisaged to become globally ubiquitous in the foreseeable future. Because of their ability to emulate the electromechanical properties of mammalian skeletal muscle in terms of both electroactuation strain, frequency range and blocking stress, DEs are routinely referred to as artificial muscle, although it must be recognized that DEs do not possess the same electrochemical
actuation mechanism or hierarchical fibrous organization as skeletal muscle.\textsuperscript{28} In fact, unlike skeletal muscle (which actuates in linear fashion), DEs tend to exhibit isotropic electro-actuation unless they are constrained to respond in a more directed manner.\textsuperscript{29} As described in Section IV, efforts to enhance the anisotropic electroactuation of DEs have relied on the incorporation of fibrous trusses,\textsuperscript{30-34} which affect electroactuation and mechanical properties. Another approach that shows promise in this vein is the use of aligned carbon nanotube electrodes.\textsuperscript{35}

Most studies of DEs focus on the electromechanical properties of elastomers derived from acrylics, silicones, polyurethanes, or natural/synthetic rubber.\textsuperscript{36} Of these, the double-sided adhesive tape based on an acrylic elastomer (VHB commercialized by 3M Co.) has evolved into the gold standard\textsuperscript{37} for DEs by receiving significant attention worldwide due to its favorable combination of electromechanical properties and convenient availability. However, in addition to its proprietary chemistry, a drawback of VHB that thwarts materials development is that it is manufactured in only two thicknesses: 1 mm and 0.5 mm. Greater design flexibility is achieved through the use of silicone and polydiene-based elastomers, whose properties can be tailored through chemical means. A critical consideration that has plagued the technological development of DEs since their introduction as electroresponsive materials relates to the high electric fields needed to promote electroactuation. For the elastomers mentioned thus far, actuation field strengths typically range from 10 to 300 kV/mm. To overcome this practical complication, specimens are frequently subjected to uniaxial or biaxial mechanical prestrain to reduce specimen thickness (and thus limit the voltage required to ensure safe operation). Three other non-negligible consequences accompany the mechanical prestraining of DEs prior
to electroactuation: (1) the elastomer network becomes stretched, thereby causing the (electro)mechanical properties of the DE to change;\textsuperscript{38,39} (2) the prestrained elastomer eventually undergoes stress relaxation as its network evolves over time; and (3) mechanical prestraining requires the use of a rigid load frame that severely compromises the promising lightweight and flexible features of DEs. The DE designs considered below aim to improve the performance of DEs and, in some cases, eliminate the need for mechanical prestrain.

II. ELECTROACTUATION

A. Operating Principle

Dielectric elastomers are capacitors that consist of a soft dielectric medium sandwiched between two compliant electrodes, as schematically depicted in Figure 2.1. When an electrostatic potential (\(\Phi\)) is applied across the capacitor, the attractive force between the oppositely-charged electrodes creates a compressive stress (referred to as a Maxwell stress, \(\sigma_M\)) that is sufficiently large to induce substantial compression on the elastomer film. Since this electroactuation process is considered to be isochoric, transverse compression along the \(z\) direction identified in Figure 2.1 promotes in-plane (lateral) film expansion. While the buildup of repulsive like charges along each of the electrodes further promotes lateral expansion of the DE, we only consider the effect of Maxwell compression in the following derivation. According to the continuum model proposed by Pelrine \textit{et al.},\textsuperscript{37} \(\sigma_M\) acting normal to the film surface can be expressed as \((1/A_{xy})(d\Phi/dH)\), where \(A_{xy}\) is the active surface area being electrically stimulated and \(H\) is the DE film thickness. For a parallel-plate capacitor such as the one illustrated in Figure 2.1, \(\Phi = Q^2/(2C)\), where \(Q\) is the electrical charge on the electrodes
and the capacitance (C) is given by \( \varepsilon_0 \varepsilon A_{xy}/H \). Here, \( \varepsilon_0 \) corresponds to the dielectric permittivity of vacuum \((8.85 \times 10^{-12} \text{ F/m})\), and \( \varepsilon \) denotes the relative dielectric permittivity (dielectric constant) of the elastomer. The change in potential (d\(\Phi\)) accompanying simultaneous changes in \(H\) and \(A_{xy}\) during electroactuation are determined from

\[
d \Phi = \frac{Q^2}{2} \frac{\text{d}H}{A_{xy}} \frac{H A_{xy}}{A_{xy}^2} \frac{\text{d}A_{xy}}{A_{xy}^2}.
\]

Because of isochoric electroactuation, \(dV = z\text{d}A_{xy} + A_{xy}\text{d}z = 0\), in which case Eq. 1 simplifies to

\[
d = \frac{Q^2}{2} \frac{\text{d}H}{A_{xy}}
\]

(2)

Since the magnitude of the electric field (E) can be written as \(Q/\varepsilon_0 \varepsilon A_{xy}\), it follows that, after algebraic substitution and rearrangement of Eq. 2, \(\sigma_M = \varepsilon_0 \varepsilon E^2\) for an ideal DE. If the DE does not behave ideally, then alternative electromechanical analyses must be considered. Since \(E(=\Phi/H)\) changes (as do \(\Phi\) and \(H\)) during electroactuation, it is common practice (as adopted here) to monitor the nominal \(E\) given by \(\Phi/H_0\), where \(H_0\) denotes the pre-actuation DE film thickness.

By assuming elastic deformation at relatively low electroactuation strains (less than \(\sim 20\%\)), the corresponding transverse strain (s_z) can be considered linearly dependent on \(\sigma_M\) and can therefore be determined directly from Hooke's law as \(\varepsilon_0 \varepsilon E^2/Y\), where \(Y\) is Young's modulus. For the DEs of interest here, large strains beyond the limit of Hookean behavior are frequently encountered, in which case \(Y\) becomes a function of strain and \(s_z\) is discerned from constitutive
equations stemming from the presumption that electroactuation proceeds isochorically. Within a 3D orthogonal coordinate system, the in-plane and transverse strains must therefore satisfy the condition that \( \lambda_x \lambda_y \lambda_z = 1 \), where \( \lambda \) is the extension ratio, which is related to strain by \( \lambda = s + 1 \). If electroactuation proceeds isotropically in-plane, then \( \lambda_x = \lambda_y = \lambda_{xy} \) (1D lateral extension) and \( \lambda_z = H/H_0 = \lambda_{xy}^{-2} \). Since DEs are routinely measured in a circular test frame, however, the in-plane electroactuation response is radial, thereby producing a 2D areal extension (\( \lambda_a \)). In this case, it can be shown that \( \lambda_z = \lambda_a^{-1} \). While the electromechanical stress-strain behavior for DE actuators has been reported in the context of various hyperelastic (e.g., Mooney-Rivlin,\(^{41}\) Ogden,\(^{42}\) Yeoh,\(^{43}\) Neo-Hookean,\(^{44}\) and slip-tube\(^{45}\)) models, two other metrics are commonly employed to measure the performance of ideal DEs as actuators and generators. The first is the elastic energy storage density (\( W \)), which describes the work generated per actuation cycle per unit volume of DE and is defined\(^37\) by \( -\sigma M \ln \lambda_z \). The second metric is the electromechanical coupling efficiency (\( k^2 \)), a measure of the ratio of stored mechanical energy to input electrical energy. It provides the energy conversion efficiency and can be conveniently expressed\(^37\) as \( 1 - \lambda_z^2 \), assuming that \( \varepsilon \) does not change during electroactuation. In this limit, the only route by which to achieve high efficiency levels is to generate large transverse electroactuation strains.

On the basis of the electromechanical model proposed by Pelrine et al.\(^{37}\) for ideal DEs, three tunable parameters can be used to alter the electroactuation behavior of DEs: (1) the compressive modulus (or, more generally, the softness) of the DE, (2) the dielectric constant of the DE, and (3) the electric field strength of poling (related to the thickness of the DE film at constant \( \Phi \)). Not surprisingly, the role of each of these parameters has been extensively
interrogated and, in the process, additional factors regarding DE characteristics, such as mechanical toughness, fatigue resistance, and cyclic hysteresis, have also been found to influence the overall performance of DEs. While the first two considerations are material properties that are not necessarily independent, the last one relates to the electroactuation process. As previously mentioned, a reduction in DE film thickness can be achieved in one of two ways. The first is to fabricate thin elastomer films, but this strategy is severely limited in practice. Decreasing $H_0$ is accompanied by the development of defects that become increasingly more significant and that render premature device failure by depressing the dielectric breakdown strength. To circumvent this shortcoming, rigid load supports are widely employed as a means by which to induce mechanical prestrain in relatively thick films and retain film integrity while reducing thickness prior to electroactuation. However, the application of mechanical prestrain to achieve large actuation strains thwarts the practical benefits of DEs. Although prestrain increases DE capacitance, breakdown strength, and electromechanical modulus, designs incorporating rigid supports add substantial mass to an actuator and reduce the power to weight ratio. Moreover, DE elastomer films subjected to prolonged prestrain are prone to stress relaxation, which leads to premature failure and reduced operational lifetimes.\textsuperscript{45} Ongoing attempts to altogether eliminate the need for mechanical prestrain have yielded new material designs, as described in detail later.

\section*{B. Electromechanical Instability}

An important feature of DE electroactuation is the possibility of an electromechanical instability (EMI), a type of "snap-through" instability, which occurs as a drastic thinning when
the electrostatic Maxwell stress exceeds the mechanical resistance of the DE elastomer. This phenomenon causes failure in DEs that reach their dielectric breakdown strength, but is also responsible for massive actuation strains in DEs with high breakdown strength and appropriate non-linear mechanics. To better understand the conditions associated with EMI, we first describe the compressive stress-strain behavior of different DE elastomers and then translate these results into analogous electromechanical responses. As depicted in Figure 2.2a wherein true stress ($\sigma$) is provided as a function of $\lambda_a$, an initially relaxed conventional elastomer undergoes relatively gradual strain stiffening upon deformation, since the network segments between crosslinks can only undergo finite extension. If the elastomer is first subjected to equibiaxial strain (to, for example, introduce mechanical prestrain), $\sigma$ is seen in Figure 2.2a to become much more strongly dependent on $\lambda_a$ and the extent of strain stiffening increases substantially for a given $\lambda_a$, since the network segments are stretched prior to further deformation. Included for comparison in Figure 2.2a are results from a relatively new genre of elastomers: bottlebrush elastomers (BBEs). Unlike traditional elastomers, this class of chemically-crosslinked materials contains side chains densely grafted along and thereby enlarging the polymer backbone. Since neighboring side chains experience steric repulsion the magnitude of which depends on their length and grafted density, the distance between crosslinks is increased so that BBEs are inherently swollen and thus prestrained at the molecular level, and their mechanical behavior effectively combines the responses from relaxed and strained elastomers (cf. Figure 2.2a).

As alluded to earlier, the electromechanical properties of a DE are strongly dependent on its mechanical properties. The relationship that serves to couple these properties responsible
for electroactuation can be expressed as

\[ E(z) = z \sqrt{\left| \frac{\lambda}{\lambda_0} \right|} \]  

(3)

As electroactuation proceeds, the DE film thins until failure when either the limit of mechanical strain or dielectric breakdown is reached. Mechanically or molecularly strained elastomers portrayed in Figure 2.2a are expected in Figure 2.2b to fail by dielectric breakdown, the magnitude of which depends on several material- and process-related considerations, whereas conventional elastomers possessing relaxed chain segments exhibit a unique feature during electroactuation. At the maximum in E evident at the value identified as \( \lambda_{\text{aEMI}} \) in Figure 2.2b, the DE film undergoes an EMI, which induces a snap-through response as the DE compresses under isofield conditions to the point of dielectric breakdown. This instability is predicted\(^{46}\) to occur at \( \lambda_{\text{aEMI}} = 1.59 \). Theoretical predictions indicate that, due to the nonlinear mechanical properties of hyperelastic materials, a DE might be capable of surviving the EMI and achieving a large, stable actuation state. To avoid encountering the EMI, a conventional DE can be fastened to a load frame and mechanically prestrained as discussed above, or it can be swollen with a second component in conjunction with mechanical prestraining. In the particular case of BBEs, the EMI can likewise be circumvented by judicious choice of molecular stretching, which is governed by the length and graft density of the side chains chemically attached to the polymer backbone.\(^{39}\) In the following section, we discuss several new material designs introduced at different length scales with the intention of enhancing the performance of DE electroactuation.
III. MULTISCALE MATERIAL DESIGN

A. Macroscopic length scales

Unless purposefully restricted, electroactuation occurs isotropically, which means that the electrical energy introduced into a DE is expended to generate expansion in all directions normal to the Maxwell stress. For many intended applications, however, DE electroactuation should be conducted along a specific direction to ensure efficient energy utilization. As schematically depicted in Figure 2.3a, directional, or anisotropic, electroactuation can be realized through the precise arrangement of fibers within a DE matrix prior to electrical stimulation. Incorporation of polyamide (PA) fibers into a chemically-crosslinked silicone DE have been reported to serve as trusses that can hold mechanical prestrain and generate as much as 35% linear strain. Similarly unidirectional constraint using oriented PA or carbon fibers has resulted in 25% or 28% linear actuation strain, respectively, at the onset of dielectric breakdown. In a cylindrical geometry, linear electroactuation increases to 36%. Subramani et al. have previously established that addition of multifilament polyurethane (PU) fibers to the VHB acrylic elastomer (cf. Figure 2.3b) without mechanical prestrain promotes two essential DE alterations. The first is that the dielectric properties of the composite DE change abruptly. Figure 2.4 confirms that addition of PU fibers at surprisingly low fiber contents in the elastomer under both prestrain-free and prestrain conditions generates a large and systematic increase in \( \varepsilon \), followed by a plateau that approaches \( \varepsilon \) of the PU fibers (≈ 7). The Maxwell Garnett approximation, one of several models proposed to predict \( \varepsilon \) for heterogeneous composites, is given by
\[
\varepsilon_c = \varepsilon_m + \varepsilon_m \phi \left[ \frac{(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + (1 - \phi) N(\varepsilon_f - \varepsilon_m)} \right]
\]

(4)

where \(\varepsilon_c, \varepsilon_m\) and \(\varepsilon_f\) correspond to the dielectric constants of the composite, matrix and fiber reinforcements, respectively, \(\phi\) denotes the fiber volume percent, and \(N\) accounts for the cylindrical fiber shape. Nonlinear regression of Eq. 4 to all the data presented in Figure 2.4 yields a single curve that favorably reflects the data and yields \(\varepsilon_f = 7.55 \pm 0.62\) in the limit as \(\phi \rightarrow 1.0\).

The second noteworthy outcome achieved by incorporating fibers in a DE matrix is the development of composition-dependent anisotropic electroactuation. Electroactuation strains measured for the virgin elastomer, as well as composites along orthogonal directions relative to the fiber direction, are displayed in Figure 2.5a and demonstrate that (i) the addition of fibers initially serves to improve electroactuation at reduced field strengths, and (ii) electroactuation is more pronounced perpendicular to the fiber direction than along the fiber axis. The first observation is consistent with the increase in \(\varepsilon\) evident in Figure 2.4, whereas the second is related to differences in modulus (which is higher along the fiber axis and lower in the normal direction). While a mechanical anisotropy can be calculated from the ratio of elastic moduli in the \(x\) and \(y\) directions identified in Figure 2.3a, an equivalent electromechanical anisotropy can be determined from \(s_x/s_y\). These anisotropy values are provided as a function of fiber content in Figure 2.5b and reveal that the electromechanical anisotropy consistently exceeds the mechanical anisotropy for the case of PU fibers embedded in a prestrain-free elastomer matrix. A dielectric enhancement factor (\(\xi\)) defined as the ratio of electromechanical to mechanical anisotropy constitutes a quantitative measure of the extent to
which anisotropic electroactuation surpasses anisotropic compression and is included as an inset in Figure 2.5b. As mentioned at the start of this section, the principal motivation for inducing directed electroactuation is to improve energy efficiency. Values of the electromechanical efficiency \(k^2\) plotted in Figure 2.5c confirm that the incorporation of fibers unequivocally achieves this objective by greatly improving the electro-mechanical efficiency from \(\sim 50\%\) to 70-80\%. In addition to the use of fibers, anisotropic electroactuation has been realized through the use of aligned crystals in the elastomer matrix\(^{34}\) or oriented carbon nanotube electrodes.\(^{35}\)

**B. Mesoscopic length scales**

Conventional elastomers employed as DEs rely on chemically-crosslinked polymer networks whose properties rely largely on chemical specificity (of both the network-forming polymer and crosslinking agent) and network topology, which includes the molecular weight of segments between crosslinks (or, alternatively, the crosslink density). Many reported studies of pre-made DEs (e.g., the VHB acrylic elastomer) or DEs crosslinked according to a manufacturer's recipe (e.g., silicone elastomers) focus almost exclusively on the electromechanical properties of such unstructured materials. The efforts of Shankar *et al.*\(^{50}\) have sought to introduce a new strategy into the development of DEs possessing considerable tunability. Their approach exploits the unique thermomechanical properties of styrenic thermoplastic elastomers (TPEs) based on ABA triblock copolymers, each consisting of glass-forming (styrenic) A endblocks and a rubbery (olefinic) B midblock.\(^{51}\) Due to the inherent thermodynamic incompatibility between the chemically-dissimilar A and B blocks, block
copolymer molecules can spontaneously microphase-separate and self-assemble into various nanoscale morphologies that frequently reflect molecular composition.\textsuperscript{52,53} Since commercial TPE triblock copolymers typically possess 0.30-0.33 wt% A, they routinely order into spherical A micelles positioned on a body- or face-centered cubic lattice in a B matrix or cylindrical A micelles arranged on a hexagonal lattice in a B matrix. To improve the elasticity of such TPEs and correspondingly reduce their modulus, a low-volatility, midblock-selective oil can be incorporated to yield a stable thermoplastic elastomer gel (TPEG).\textsuperscript{54} The ternary morphology diagram displayed in Figure 2.6a illustrates the rich morphological behavior of TPEGs composed of a poly[styrene-\textit{b}-(ethylene-co-propylene)-\textit{b}-styrene) (SEPS) triblock copolymer modified with a midblock-selective mineral oil (MO) and an endblock-selective homopolystyrene (hPS).\textsuperscript{55} From the standpoint of DEs, only binary (oil-containing) TPEGs are considered further, and a transmission electron microscopy (TEM) image of a TPEG consisting of glassy micelles in a swollen rubber matrix is included in Figure 2.6a.

A critical difference between ABA triblock copolymers and their simpler AB diblock copolymer analogs is that the former not only microphase-separate but also develop molecular networks since an ABA molecule is capable of depositing its endblocks into two different glassy microdomains (\textit{e.g.}, micelles), which consequently serve as physical crosslink sites.\textsuperscript{56,57} The fraction of these network-forming (bridged) molecules in neat TPEs is dependent on molecular composition, ranging from just over 40\% in lamellae-forming copolymers to over 60\% in sphere-forming copolymers, according to independent experimental measurements,\textsuperscript{58} theoretical predictions\textsuperscript{59} and simulation results.\textsuperscript{60} In the case of TPEGs, several transitions must be carefully considered in terms of both application and processing. Under isothermal
application conditions, a TPEG exhibiting a discrete micellar morphology must possess a sufficiently high copolymer concentration to exceed its critical micelle concentration (to permit the formation of micelles) and critical gel concentration (to permit the formation of midblock bridges). The Monte Carlo simulations presented in Figure 2.6b reveal that the fraction of midblock bridges in a midblock-swollen ABA copolymer with 20% A increases upon incorporation of oil until the network collapses in close proximity to the critical gel concentration. Upon heating at constant composition during processing, a TPEG undergoes measurable modulus reductions at the upper glass transition temperature (where endblock pullout can occur) and the order-disorder transition temperature (where an ordered copolymer morphology becomes disordered). The mechanical (and, by inference, electromechanical) properties of TPEGs can be controllably modified by changing the molecular chemistry, composition and mass of the TPE copolymer, as well as the concentration, selectivity and viscosity of the midblock-selective diluent.

While a high-viscosity, midblock-selective, saturated tackifying resin can be incorporated into TPEs to alter mechanical properties (e.g., adhesion), the resultant blends often exhibit viscoelastic behavior instead of the elastomeric behavior required for most DE applications. Insofar as the tackifying resin is miscible with a low-viscosity, midblock-selective oil, ternary blends (composed of a copolymer and two midblock-selective diluents) yield TPEGs possessing highly tailorable mechanical properties capable of evincing time-composition rheological equivalence. For most TPEGs targeted for use as DEs, a single, low-viscosity diluent added at different concentrations normally provides a sufficiently wide range of electroactuation responses without resorting to a third component. The results included in
Figures 2.7a and 2.7b demonstrate the versatile electroactuation behavior of styrenic and acrylic TPEGs, respectively, varying in copolymer content. Interestingly, while the styrenic TPEGs require mechanical prestrain as described earlier, the acrylic TPEGs do not because of their higher ε, a consequence of both copolymer chemistry and the diluent employed. By assuming the electromechanical model derived in Section IIA, the electroactuation strains portrayed in Figure 2.7a can be translated into the corresponding electromechanical stress-strain behavior, which is displayed in Figure 2.7c. Upon further analysis, these results yield the electromechanical moduli (Y_E) as functions of copolymer concentration (C) and mechanical prestrain in Figure 2.7d. The scaling dependence of Y_E on C appears quantitatively similar to that of the mechanical modulus and is in favorable agreement with previous experimental measurements and theoretical predictions. As new diluents and/or functional moieties are introduced into TPEs to further modify bulk properties, new opportunities arise regarding the development of tunable EAPs. Sulfonation of the midblock in a TPE pentablock copolymer, for instance, has permitted fabrication of TPEG-based IPMCs, which, as alluded to earlier, rely on ion migration in a polar diluent and subsequent heterogeneous swelling for bending electroactuation.

C. Nanoscopic length scales

Although the material designs detailed in the previous sections afford alternative strategies for designing DEs with tailorable properties, most ongoing studies of DEs rely on the traditional use of chemically-crosslinked acrylic and silicone elastomers due largely to the ease by which these materials can be obtained or produced. In this section, we explore how these
materials can be controllably modified at the nanoscale to yield DEs with superior electroactuation properties. In the case of acrylic elastomers (of the VHB genre), Ha et al.\textsuperscript{70} have proposed a simple, but clever, scheme by which to introduce mechanical prestrain into a DE without the need for a cumbersome external frame during application. They have demonstrated that, by first mechanically prestraining a previously crosslinked acrylic elastomer and then infusing a second chemically-compatible and -crosslinkable species into the stretched elastomer, the resulting DE is capable of retaining a concentration-dependent degree of its prestrained state when relaxed. During free-standing electroactuation, these so-called "binetwork" DEs consist of a relatively rigid crosslinked network within an ordinarily soft matrix and are capable of achieving strains beyond 220\%, as evidenced by the electroactuation curves presented in Figure 2.8a, thereby providing remarkable improvement over the parent elastomer. While the VHB elastomers are readily accessible and convenient for electroactuation studies, Pei and co-workers\textsuperscript{71} have also established that designer photocrosslinked acrylic elastomers can be rationally synthesized as prestrain-free DEs that altogether avoid the EMI discussed earlier in Section IIB (cf. Figure 2.2b). Their target electromechanical properties are guided by the theoretical predictions of Zhao and Suo,\textsuperscript{46} who first identified the EMI and the typical responses of DEs. The resultant DEs generated from acrylic cocktails containing varying concentrations of 1,6-hexanediol diacrylate and isodecyl acrylate are capable of attaining giant electroactuation strains, as illustrated in Figure 2.8b, without any need for prestrain provided by mechanical or otherwise means. The specially designed acrylics have been implemented in ultra-thin DE devices that operate with large strains at voltages as low as 600 V\textsuperscript{72}. 


Another route by which to alter the electroactuation properties of DEs and eliminate the need for external prestrain is to design prestrain directly into the polymer network. As indicated in Figure 2.2b, this can be accomplished through the synthesis of BBEs, which consist of inherently stretched networks due to steric hindrance of the side chains grafted onto the polymer backbone, as schematically depicted in the inset of Figure 2.9a. Daniel et al.\(^7\) have recently reported that silicone BBEs possessing variable side chain lengths and crosslink densities can be systematically generated with moduli as low as \(~100\) Pa and elongations at break as high as \(~10\). These materials have also been found\(^39\) to exhibit remarkable electromechanical properties, as confirmed by the results acquired from the inflatable diaphragm tests shown in Figure 2.9a. In this configuration, the nominal electric field can be written as

\[
E = \sqrt{\frac{2}{z} \frac{PR}{4H_0} \sqrt{\frac{1}{z} \frac{1}{\lambda_a}}} \tag{5}
\]

where \(P\) denotes the blowing pressure, applied to regulate the electroactuation direction, and \(R\) is the radius of the active area of the DE film. Predictions from Eq. 5 are seen in Figure 2.9b to compare favorably with experimental results obtained from two series of silicone BBEs with different segment lengths between crosslinks (\(n_x\)) and side chain lengths (\(n_{sc}\)). When \(n_x = 200\), the electroactuation response is dictated by the value of \(n_{sc}\): BBEs with \(n_{sc} = 28\) reveal no evidence of the EMI as they undergo voltage-induced stretching to \(\lambda_a \approx 3.2\) before they fail by dielectric breakdown, whereas those with \(n_{sc} = 14\) encounter the EMI at \(\lambda_a \approx 1.6\) and undergo isofield snap-through up to \(\lambda_a \approx 3.8\) before ultimately failing at \(\lambda_a \approx 4.0\) (~300% strain). A
reduction in \( n_x \) at constant \( n_{sc} (= 14) \) is observed to increase the electric field required for electroactuation to a given extension and ultimately eliminate the EMI altogether. Another independent parameter that permits simultaneous control over the modulus and strain-stiffening behavior is the graft density, which is regulated by the number of repeat units between side chains (\( n_g \)). In Figure 2.9, \( n_g = 1 \).

**IV. CONCLUSIONS**

Dielectric elastomers afford excellent opportunities for the development of lightweight and tough actuators required in a diverse assortment of contemporary technologies focused on soft robotic, microfluidic, haptic, optical, and biomedical devices. Since the initial studies of various elastomers capable of electroactuation, numerous advances in materials design have yielded DEs that possess fiber-directed electroactuation, highly tunable properties and molecular characteristics that eliminate the need for mechanical prestrain, which has greatly hindered commercialization of DEs since their inception. Strategies involving composite materials have been explored, but have been successful primarily as electromechanical transducers for energy capture. Composites with high permittivity fillers have been less successful as artificial muscles due primarily to decreases in dielectric strength and increases in stiffness. Excluding hybrid systems containing high-dielectric (nano)fillers,\(^{74-77}\) DEs with and without mechanical prestrain are now capable of exhibiting a broad range of maximum actuation responses at significantly lower nominal electric fields as new DE designs have been introduced and electromechanical efficiencies have been improved. A compilation of current achievements in this regard is displayed for comparative purposes in Figure 2.10. For DEs to become an increasingly commercially viable option, mechanical prestrain must be completely
eliminated and the electric field necessary to induce electroactuation must be reduced further. While the first requirement has now been successfully realized, the second remains an ongoing challenge to most likely be accomplished through a synergistic combination of both physical and chemical means.

V. ACKNOWLEDGMENTS

D. P. A. is grateful to Becton-Dickinson Technologies and the Eastman Chemical Company for financial support.
VI. REFERENCES


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Figure 2.1 Schematic diagram of the mechanism by which electroactuation occurs in dielectric elastomers (DEs). Most electroactuation measurements are conducted so that compression of a DE by oppositely-charged compliant electrodes results in the development of a normal Maxwell stress ($\sigma_M$) that promotes transverse thinning (along $z$) and lateral expansion (along $x$ and $y$ in Cartesian coordinates, but radially in a conventional circular test configuration).
Figure 2.2  Illustrative dependence of (a) true compressive stress ($\sigma$) and (b) nominal electric field (E) on the area extension ratio ($\lambda_a$) for three specific elastomer types (color-coded): a conventional elastomer (black), a mechanically-prestrained elastomer (blue) and a bottlebrush elastomer (BBE, green). The topologies of these different elastomers are depicted in (a), and the electromechanical curves provided in (b) are generated from those in (a) by Eq. 3 in the text. The dielectric breakdown curve (red) and the electromechanical instability (EMI) are also identified in (b). (Adapted from ref. 39 with permission from Wily & Sons.)
Figure 2.3 In (a), a schematic illustration of a DE modified through the incorporation of fibers aligned in parallel to induce anisotropic (electro)mechanical properties. A corresponding cross-sectional scanning electron microscopy (SEM) image of the VHB acrylic elastomer containing multifilament polyurethane (PU) fibers (each fiber measuring 40-50 μm in diameter) is included in (b). (Adapted from ref. 33 with permission from Wiley & Sons.)
Figure 2.4 Measured values of the dielectric constant (ε) for VHB acrylic elastomers containing oriented PU fibers as functions of fiber volume percent (φ) and equibiaxial mechanical prestrain (in %): 0 (black), 100 (red) and 200 (blue). The solid line corresponds to a nonlinear regression of Eq. 4 (the Maxwell Garnett model) to all the data. (Adapted from ref. 33 with permission from Wily & Sons.)
Figure 2.5 (a) Anisotropic linear electroactuation strains measured along the x- (open symbols) and y- (filled symbols) directions identified in Figure 2.3a for acrylic elastomer composites containing 0.7 (blue diamonds) and 5.2 (red triangles) vol% PU fibers. Included for comparison are isotropic results (●) acquired from the neat elastomer. The solid lines serve as guides for the eye. (b) Electromechanical (□) and mechanical (■) anisotropy values discerned as a function of φ from the ratio of orthogonal Young's moduli (Yₓ/Yᵧ) and electroactuation strains (sₓ/sᵧ) evaluated at E = 85 kV/mm [dashed vertical line in (a)], respectively. The corresponding dielectric enhancement factor (ξ) is provided in the inset. The solid lines are linear regressions to the data. (c) Dependence of the electromechanical efficiency (k²) on φ at the same electric field as in (b). (Adapted from ref. 33 with permission from Wily & Sons.)
Figure 2.6 In (a), a ternary morphology diagram generated at 25°C from synchrotron small-angle X-ray scattering and illustrating the various nanostructures that develop in blends of a TPE (SEPS copolymer) with a midblock-selective mineral oil (MO) and/or an endblock-selective homopolystyrene (hPS). The nanostructure schematics are color-matched with the experimental results. A TEM image of a MO-rich SEPS/MO binary blend possessing glassy styrenic micelles (stained to appear dark) dispersed in a swollen rubber matrix is included as an inset [Scalebar = 50 nm]. The fraction of bridged midblocks discerned from Monte Carlo simulations for a midblock-swollen ABA copolymer with 20% A-endblocks is presented as a function of diluent content in (b).62 (The morphology diagram in (a) is adapted from ref. 55 with permission from the American Chemical Society.)
Figure 2.7 Electroactuation behavior of (a) styrenic and (b) acrylic TPEGs containing MO and dioctyl phthalate (DOP) diluents, respectively, as functions of copolymer content (labeled) and E. The solid lines serve as guides for the eye. Electromechanical stress-strain curves generated from the electroactuation results in (a) [wherein the DEs are equibiaxially prestrained to 300%] according to the model proposed\textsuperscript{39} for an ideal DE are supplied in (c). Corresponding mechanical ($Y_C$) and electromechanical ($Y_E$) modulus values extracted from results such as those in (c) for styrenic TPEGs are displayed as a function of copolymer concentration (C) in (d) for different levels of equibiaxial prestrain (labeled and color-coded). (Adapted from refs. 38 and 66 with permission from Wily & Sons.)
Figure 2.8 In (a), the electroactuation behavior of binetwork DEs composed of the VHB (4910) acrylic elastomer infused with poly(1,6-hexanediol diacrylate) at different crosslink loadings (labeled and color-coded) to avoid additional mechanical prestrain during electroactuation. In (b), electroactuation responses of photocrosslinked acrylic elastomers specifically synthesized with different levels of 1,6-hexanediol diacrylate (labeled) to avoid the predicted\(^46\) EMI and thus yield giant electroactuation strains. Corresponding results obtained from the VHB (4905) acrylic elastomer equibiaxially prestrained to 300% (●) are included for comparison in (b). (Adapted from refs. 70 and 71 with permission from Wiley & Sons.)
Figure 2.9 In (a), electroactuation of a silicone BBE ($n_x = 200$ and $n_{sc} = 14$) constrained in an inflatable diaphragm test configuration presented at different field strengths (labeled with $\lambda_a$ values). A schematic illustration of BBEs depicting the grafted side chains that sterically hinder and thus inherently strain the chemically-crosslinked polymer network is included in the inset. Corresponding extension ratios extracted from measurements such as those in (a) are provided in (b) for silicone BBEs with $n_x = 200$ at two values of $n_{sc}$: 14 (Δ, solid line) and 28 (○, dashed line). Included in (b) are results measured from BBEs with $n_{sc} = 14$ at different values of $n_x$ (labeled and color-coded). (Adapted from ref. 39 with permission from Wily & Sons.)
Figure 2.10  Overview of maximum electroactuation strains reported for DEs prepared from TPEGs (black circles), acrylic elastomers (blue triangles) and silicone elastomers (red diamonds) subjected to mechanical prestrain (open symbols) and prestrain-free (filled symbols). The broad range of values evident here is due to a wide variety of chemical constitutions and measurement conditions (e.g., prestrain level and film thickness).
Olefinic Thermoplastic Elastomer Gels: Combining Polymer Crystallization and Microphase Separation in a Selective Solvent

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Since selectively-swollen thermoplastic elastomer gels (TPEGs) afford a wide range of beneficial properties that open new doors to developing elastomer-based technologies, we examine the unique structure-property behavior of TPEGs composed of olefinic block copolymers (OBCs) in this study. Unlike their styrenic counterparts typically possessing two chemically different blocks, this class of multiblock copolymers consists of linear polyethylene hard blocks and poly(ethylene-co-\(\alpha\)-octene) soft blocks, in which case microphase separation between the hard and soft blocks is accompanied by crystallization of the hard blocks. Here, we prepare olefinic TPEGs (OTPEGs) through the incorporation of a primarily aliphatic oil that selectively swells the soft block, and investigate the resultant morphological features through the use of polarized light microscopy and small-/wide-angle x-ray scattering. These features are correlated with thermal and mechanical property measurements from calorimetry, rheology and extensiometry to elucidate the roles of crystallization and self-assembly on gel...
characteristics and establish useful structure-property relationships.

Elastomeric materials are becoming increasingly pervasive in both academic research and commercial technologies due mainly to their inherent durability and stretchability. Contemporary applications benefiting tremendously from the properties of such soft materials include biocompatible sensors for health monitoring,\textsuperscript{1} microfluidic platforms,\textsuperscript{2} and stretchable electronic devices.\textsuperscript{3,4} Traditional elastomers derive from chemically-crosslinked, low-$T_g$ homopolymers, and exhibit well-described mechanical properties.\textsuperscript{5} Recent studies focused on the development of so-called "bottlebrush" elastomers reveal\textsuperscript{6} that the properties of such materials can be further tailored at the molecular level by independently controlling the crosslink density, the graft density along the polymer backbone, and the length of the grafts. Such materials are particularly suitable as dielectric elastomers since they actuate to ultrahigh strains ($> 300\%$) at very low electric fields ($< 10$ kV/mm) without the need for mechanical prestrain.\textsuperscript{7} A drawback to chemically-crosslinked elastomers, however, is that their network is permanent, in which case they must be used as-prepared during their application lifetime (and beyond) or sent to landfills upon their end-use. Thermoplastic elastomers (TPEs) provide a recyclable and reprocessable alternative for soft and stretchy materials. The simplest block copolymer architecture displaying TPE behavior is an ABA triblock copolymer possessing glassy or semi-crystalline endblocks and a rubbery midblock.\textsuperscript{8} Upon microphase separation of the copolymer molecules, the A-rich microdomains serve as physical crosslinks to stabilize the B-rich molecular network.\textsuperscript{9}

Independent efforts have demonstrated that the properties of TPEs can be chemically\textsuperscript{10} or physically\textsuperscript{11} modified to achieve specific properties, such as amphiphilicity.\textsuperscript{12} One approach
by which to regulate the mechanical properties of TPEs is through the physical incorporation of a midblock-selective solvent. Such materials, collectively known as thermoplastic elastomer gels (TPEGs), exhibit highly tunable properties that make them attractive in adhesive,\textsuperscript{13} electroelastomeric,\textsuperscript{14} flextronic,\textsuperscript{15} microfluidic,\textsuperscript{16} and photovoltaic\textsuperscript{17} applications. Most of the TPEs employed for this purpose derive from styrenic copolymers with a polyolefin midblock selectively swollen with an aliphatic oil, although the principle has been extended to acrylic TPEs.\textsuperscript{18} In these previous studies, the parent TPE has been an ABA triblock copolymer that typically requires specialized synthetic routes.\textsuperscript{19,20} Such reactions must be performed under specific conditions and, in some cases, with relatively low-yield catalysts that compromise economic viability. A recent development in TPE synthetic design employs a "chain-shuttling" catalyst to yield multiblock copolymers with linear polyethylene hard blocks and poly(ethylene-\textit{co}-\textit{\alpha}-octene) soft blocks.\textsuperscript{21-25} In this one-pot approach, two catalysts with different branching selectivities are alternated to yield olefinic block copolymers (OBCs) with polydispersities measuring 1.9–2.1, according to the manufacturer. Since the continuous process generates thousands of chains per catalyst, this synthesis is cost effective and yields OBCs with superior properties relative to comparable random copolyolefins.\textsuperscript{21}

The objective of the present study is to couple the topics of TPEGs and OBCs through the production of olefinic TPEGs (OTPEGs) and establish their structure-property behavior, which can be controllably modified through the physical incorporation of a relatively low-molecular-weight additive. Specimen designations are expressed as OBC\textit{n}, where \textit{n} is the hard block wt\%,\textsuperscript{26} and the solvent used to swell the soft block is an aliphatic mineral oil (MO), used in previous studies of styrenic TPEGs,\textsuperscript{27,28} to permit performance comparison (examples of
which, as well as related systems, are provided in the Supplemental Information). The concentration dependence of crystal morphology in OTPEGs varying in OBC crystallinity after being isothermally crystallized at 90°C for 15 h is evident from the sequences of polarized light micrographs (PLMs) presented in Figure 3.1. These images confirm that the hard-block crystals become more clearly defined as the OBC content and, therefore, crystallinity increase. These images also reveal two other important features: (i) ill-defined crystals exist in both OTPEG series at the lowest OBC content (20 wt%), and (ii) the spherulitic crystals measure up to 50 μm across and consistently appear uniform in both size and distribution. This latter observation, which does not apply to thermally-quenched specimens, suggests that, irrespective of the hard-block content of the parent OBC, the MO is fully incorporated into the soft block microdomains using the specimen preparation protocol adopted here. To ascertain if this is indeed the case, we have performed differential scanning calorimetry (DSC) on the two OTPEG series, and a representative set of DSC thermograms acquired from materials containing 10 to 100 wt% OBC40 is provided in Figure 3.2a.

The melting endotherms of the OBC40/MO blends in Figure 3.2a are relatively broad and, unlike the neat OBC40, possess a shoulder at ~5°C below the primary peak, suggesting the existence of two crystal populations. Although the added MO selectively swells the soft blocks of the OBC, the reduction in peak melting temperature (T_m) with increasing MO content suggests solubilization of MO in the amorphous regions of the hard blocks as well. This <15°C decrease in T_m is comparable for both OBC15 and OBC40 series over the entire copolymer concentration range (cf. Figure S3.1 in the Supplemental Information). The number and length of the hard blocks, however, regulate the crystallinity (X_c), which is provided as a function of
copolymer concentration in Figure 3.2b. The overall OTPEG crystallinity ($X_{c,g}$) is calculated from the measured heat of melting relative to that for neat polyethylene (290 J/kg).\textsuperscript{30} Figure 3.2b indicates that $X_{c,g}$ increases nearly linearly with OTPEG composition in both OBC series, thereby implying that the crystallinity scales directly with the hard-block content. By correcting for the copolymer fraction in each OTPEG, the crystallinity of the polymer ($X_{c,p}$) can likewise be determined. Corresponding values of $X_{c,p}$, included in Figure 3.2b, do not generally depend on copolymer concentration, verifying that the propensity for OBC molecules to crystallize is not influenced by the presence of MO above 5 wt% OTPEG (at which $X_{c,p}$ decreases noticeably in both series). This does not necessarily mean, however, that the crystal morphology remains unaffected. To discern if the crystal structure and microdomain morphology change upon the introduction of MO, we have performed small- and wide-angle X-ray scattering (SAXS and WAXS, respectively) on OTPEGs varying in copolymer content. Due to its higher crystallinity, only OBC40-containing OTPEGs are considered further.

Lorentz-corrected scattering intensity profiles\textsuperscript{31} are presented as a function of scattering vector ($q$) in Figure 3.3a for SAXS, whereas measured intensity is plotted versus $q$ in Figure 3.3b for WAXS. In Figure 3.3a, a principal peak located at $q^*$ is detectable even at the lowest OBC40 concentration (5 wt%). The position of this peak shifts to higher $q$ with increasing OBC40 content, indicating that, since the microdomain period ($D$) is given by $2\pi/q^*$, $D$ decreases as the OTPEGs become increasingly copolymer-rich. Values of $D$, included as a function of OBC40 concentration in the inset of Figure 3.3a, indicate that their reduction is nearly linear and becomes less concentration-dependent beyond 40 wt%. For comparison, the PLM images in Figure 3.1 reveal that the hard-block crystals become more space filling as the
copolymers. The copolymer content is increased from 40 to 60 wt% OBC40. Another aspect of the SAXS profiles is the development of a second peak at \( \sim 1.75q^* \) at 20 wt% OBC40. As the OBC40 concentration is increased, this peak shifts to higher \( q \) (but retains a similar position relative to \( q^* \)) and evolves into a shoulder on the principal peak. Although this feature suggests the presence of hexagonally-packed hard-block cylinders in an oil-swollen matrix, this is not the only morphology to yield such a feature. Since we have no ancillary evidence to indicate ordered microdomains, we refrain from assigning a definitive morphology. In Figure 3.3b, complementary WAXS profiles exhibit two scattering peaks at 15.18 nm\(^{-1} \) and 16.81 nm\(^{-1} \) that identify the (110) and (200) planes of orthorhombic polyethylene crystals, respectively.\(^{32} \) While the peak intensities decrease with decreasing copolymer content, their positions do not change (unlike the amorphous halo), confirming that the hard-block crystals contain little, if any, MO.

To ensure that these materials possess load-bearing networks composed of MO-swollen soft blocks that connect hard-block microdomains, we next interrogate their rheological properties at ambient temperature. Frequency spectra of the dynamic storage modulus (\( G' \)) acquired at a strain amplitude of 0.1-1% (within the linear viscoelastic regime) are provided for OBC40-containing OTPEGs in Figure 3.4a. At concentrations above 10 wt% OBC40, \( G' \) is parallel to, and exceeds, the dynamic loss modulus (\( G'' \), not shown) over the frequency range examined, which is consistent with the Winter-Chambon criterion for polymer gel networks.\(^{33,34} \) Below 10 wt%, this is no longer the case. Corresponding values of tan \( \delta \) (\( = G''/G' \)) are plotted in Figure 3.4b to facilitate comparison of the frequency dependence. At 3.0 wt% OBC40, tan \( \delta \) generally increases and eventually exceeds unity (where \( G' = G'' \)).
indicating a solid-to-liquid transition. This behavior is attributed to the presence of copolymer flocs, instead of a contiguous network. Increasing the copolymer concentration to 5.0 and 7.5 wt% yields a less pronounced, but noticeable, dependence on frequency, with \( \tan \delta < 1 \). Values of \( \tan \delta \) measured for OTPEGs with at least 15 wt% OBC40 appear frequency-independent. These results suggest that the critical gel concentration of OBC40 in MO lies above 7.5 wt%.

Included as an inset in **Figure 3.4b** is the dependence of \( G' \) measured at 1 rad/s on copolymer concentration (C, in g/cm\(^3\)). Over the composition range examined, \( G' \sim C^n \), where \( n = 3.51 \pm 0.39 \). In contrast, \( n \approx 2.0-2.5 \) for styrenic TPEGs in this regime,\(^{35}\) in agreement with both theoretical considerations\(^{36}\) and simulations.\(^{37}\) We propose that the higher scaling exponent measured here reflects complex bridging/looping arrangements resulting from the multiblock architecture, but this interpretation requires further analysis.

Other important mechanical characteristics of TPEGs include their elasticity and durability. Styrenic TPEGs can undergo 400% uniaxial tensile strain over 100 cycles and show little (<5%) irrecoverable strain (set). Alternatively, we have found that they can be strained to 50% and continuously cycled over 5 \( \times 10^5 \) times at ambient temperature without any evidence of dynamic fatigue. Some of these TPEGs can be stretched to \(~2500\%\) before failure.\(^{38}\) To determine whether any of the present OTPEGs containing OBC40 share these remarkable attributes, we have subjected them to quasistatic tensile tests wherein either the copolymer concentration is fixed at 60 wt% and subjected to 400% cyclic strain (**Figure 3.5a**) or the strain is varied from 50 to 1000% at 60 wt% OBC40 (**Figure S3.2** in the Supplemental Information). Included in **Figure 3.5a** are values of the energy associated with the cyclic hysteresis loops for the neat OBC40 copolymer as well as the OTPEG with 60 wt% OBC40
revealing that it is consistently lower for the latter. In addition, tensile tests conducted to failure on OTPEGs ranging in copolymer concentration from 40 to 80 wt% OBC40 in Figure 3.5b demonstrate that some of these materials subjected to isothermal crystallization are capable of achieving tensile strains approaching 2000%, while the neat OBC40 copolymer can be strained to ~2900%. If the OTPEGs are quench-crystallized in water, however, they can consistently reach significantly higher elongations, nearly 4000% in the case of the OTPEG with 80 wt% OBC40. Included in the inset of Figure 3.5b are the corresponding tensile moduli, which indicate the extent to which these materials can be softened through the addition of MO. In summary, the morphological, thermal and mechanical results reported in this study establish that, like their parent OBC copolymers, 39 OTPEGs constitute an intriguing, but complex, class of semi-crystalline materials that expand the current bounds of soft elastomers by possessing tunable and, in some cases, remarkable bulk properties generated by both hard-block crystallization and microphase separation.

**Experimental Section**

The two copolymers examined here were commercial products (INFUSE 9107 and 9530 designated as OBC15 and OBC40, respectively) provided in pellet form by the Dow Chemical Company (Midland, MI). The pellets were combined in specified ratios with MO (Witco Hydrobrite 380, Crompton Corp., Petrolia, PA), and each mixture was diluted down to 5 wt% OBC in xylene. To melt the OBC and produce a solution, each mixture was heated to 125°C under reflux until it appeared transparent. Resultant solutions were quickly cast into films at ambient temperature since crystallization commenced upon cooling. The solvent was
allowed to evaporate for 5-7 d, and the resultant gels were annealed for 8-16 h under vacuum at 130°C to remove residual solvent and permit chain relaxation. A Nikon Optiphot light microscope was used to perform polarized light microscopy on gels re-melted at 130°C and pressed into thin films measuring 100 µm thick between glass slides before undergoing isothermal crystallization at 90°C for 15 h. The DSC measurements were conducted on a TA Q2000 unit operated at a heating rate of 10°C/min. For rheological, tensile and scattering analyses, samples were melt-pressed at 160°C into templates measuring 1.0 mm thick and 25 mm in diameter, and then isothermally crystallized at 90°C for at least 1 h. Dynamic rheological measurements were acquired on a TA ARES shear-controlled rheometer. Parallel plates were pressed into contact with each specimen with minimal normal force (< 50 mN). Quasistatic uniaxial tensile tests of isothermally and quench-crystallized specimens were conducted on an Instron 5943 load frame operated at a crosshead speed of 1% strain/s at ambient temperature. Simultaneous SAXS and WAXS data were collected at the Advanced Photon Source (Argonne National Laboratory) on beam line 12-ID-B according to the experimental details provided elsewhere.40

Acknowledgments

This work was supported by Becton-Dickinson Technologies and the Nonwovens Institute at North Carolina State University. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.
**Figure 3.1.** PLM images of OTPEGs containing OBC15 and OBC40 at different copolymer compositions (labeled).
Figure 3.2. In (a), DSC thermograms of OTPEGs varying in OBC40 concentration (in wt%, labeled). Crystallinities (labeled) are displayed as functions of composition in (b) for OTPEGs containing OBC15 (filled symbols) and OBC40 (open symbols). The solid lines in (b) are guides for the eye, whereas the dashed lines identify $X_{c,p}$ for the neat copolymers.
Figure 3.3. In (a) and (b), color-coded SAXS and WAXS profiles, respectively, for OTPEGs varying in OBC40 concentration (in wt%, labeled). Values of D are displayed as a function of OBC40 content in the inset in (a), and the solid lines constitute linear fits to the data.
Figure 3.4. Frequency spectra of (a) $G'$ and (b) $\tan \delta$ for OTPEGs varying in OBC40 concentration (in wt%): 3.0 (●), 5.0 (▲), 7.5 (○), 15 (△), 20 (◇), and 40 (□). Solid lines connect the data. Values of $G'(C)$ are presented along with a power-law fit to the data in the inset of (b).
Figure 3.5. Nominal stress-strain responses presented for (a) a 60 wt% OBC40 OTPEG cycled 4 times to 400% strain (labeled) and (b) OTPEGs containing different OBC40 concentrations (labeled, in wt%) for specimens subjected to isothermal and quench crystallization (thick and thin lines, respectively). Values of the energy from the cyclic hysteresis loops in (a) are provided as a function of cycle number for the OBC40 copolymer (■) and 60 wt% OBC40 OTPEG (●) in the inset (the solid lines are guides for the eye). The inset in (b) displays the tensile moduli of OTPEGs prepared by isothermal (○) and quench (■) crystallization.
References


In this Supplemental Information, we supply some additional data to complement the findings reported in the main text. We also seek to provide a more detailed comparison between the OTPEG systems discussed in the main text and related systems, most notably TPEGs derived from styrenic triblock copolymers. The first topic to be addressed focuses on the variation in the melting temperature ($T_m$) with OTPEG composition for the two material series examined. This dependence is displayed in Figure S3.1 and confirms that the thermal behavior of the two series is almost identical, which is not surprising since the variation is less than 15°C and both series contain the same crystallizable segment. Another topic to be considered here is the response of OTPEGs to progressive strain cycling. Results obtained from an OTPEG composed of 60 wt% OBC40 subjected to successive tensile strains progressively increased from 50 to 1000% are presented in Figure S3.2 and indicate growth in hysteresis as the maximum strain is increased.

The hysteresis evident in Figure S3.2 provides a good starting point for a comparison between the OTPEGs discussed in this study and conventional TPEGs derived from styrenic triblock copolymers. Since the synthetic routes to the neat copolymers are considerably different, it must be remembered that styrenic TPEGs are typically composed of low-polydispersity copolymers possessing a well-defined molecular architecture (as triblock copolymers) and amorphous blocks. In this case, the phase behavior and morphological characteristics of TPEGs is significantly more predictable,\textsuperscript{1-3} since it is directly comparable to that of neat and homopolymer-blended triblock (and diblock, for that matter) copolymers.\textsuperscript{4} Microphase separation permits the formation of glassy microdomains, which serve as physical cross-link sites to stabilize the molecular network responsible for TPEGs possessing very low
hysteresis (< 5% strain at moderate strain cycles), high fatigue resistance and giant strains up to ~2500%. Since most commercial styrenic triblock copolymers designed as TPEs possess 29-33 wt% polystyrene endblocks (although other compositions are available for specialty applications) to ensure a dispersed (spherical or cylindrical) morphology, different products commonly vary in terms of characteristics such as molecular weight and midblock composition/microstructure.

A potential drawback of styrenic TPEGs is that the endblocks can be pulled out from their glassy microdomains if the blocks are sufficiently short (and remain unentangled) or if the midblock-selective oil plasticizes the glassy endblocks. Such pullout results in "chain hopping" as endblocks migrate from one microdomain to another. This molecular mechanism can ultimately compromise the mechanical properties of the TPEG. In contrast, the OTPEGs investigated here possess both block and chain polydispersity, which can have a significant effect on morphological development and phase behavior in multiblock copolymer systems. Two main advantages of OTPEGs over styrenic TPEGs are that (i) they are capable of connecting multiple microdomains due to their multiblock architecture and (ii) they rely on crystallization, rather than vitrification, to immobilize the hard segments comprising the physical cross-links. Because of their high degree of connectivity and the presence of semi-crystalline hard blocks, the OTPEGs display considerable hysteresis upon initial deformation, but strain conditioning greatly reduces the level of hysteresis to that of styrenic TPEGs. In addition, depending on the concentration, OTPEGs can be much tougher than their styrenic counterparts, and they can, in principle, be implanted for in vivo applications.
Another important comparison to be made here is between the present moderate-polydispersity OTPEGs and conventional TPEGs derived from a low-polydispersity, semi-crystalline triblock copolymer. For this purpose, we focus on the model poly[syn-propylene-b-(ethylene-co-propylene)-b-syn-propylene] (PEPP) triblock copolymer synthesized and characterized by Deplace et al.\(^\text{10}\) In addition to the obvious difference in molecular architecture, PEPP copolymers tend to possess high molecular weights (~500 kDa) compared to both styrenic and olefinic block copolymers (~100-150 kDa). This molecular weight difference not only impacts the mechanical properties, but also the phase behavior. For example, Li et al.\(^\text{11}\) propose that, due to their relatively low molecular weight, OBCs lie near their order-disorder transition (ODT) and exhibit morphologies that are poorly ordered. On this basis, we expect that the corresponding OTPEGs are closer to their ODT and even less ordered than the parent OBCs, which is evident from our SAXS findings. From a mechanical perspective, PEPP gels exhibit better strain recovery than OTPEGs, but this comparison might reflect gel concentration or copolymer architecture or both. Semi-crystalline TPEs generally possess higher hysteresis (strain set) than glassy TPEs due to the rearrangement and formation of fiber-like crystals.

While the critical gel concentrations of OTPEGs and PEPP gels are comparable (< 10 wt%), their mechanical behavior beyond the linear viscoelastic threshold is substantially different. The PEPP gels are load-bearing and capable of giant strains (> 3000%) at concentrations below 10 wt%. In contrast, OTPEGs exhibit a precipitous drop-off in elongation at break and toughness below 30 wt% copolymer. This apparent difference is attributed to the high polydispersity of the OBC molecules and, at low copolymer concentrations (according to
our DSC results) incomplete hard-block crystallization. Unfortunately, the crystallinity values of PEPP gels have not yet been reported, and only one gel concentration has been investigated by Deplace et al.\textsuperscript{10} With this shortcoming notwithstanding, we point out that both OTPEGs and PEPP gels are more capable of blunting crack propagation than their parent TPEs. The biggest difference between the two families of TPE gels is that the OTPEGs possess greater property hysteresis due most likely to their inherent block/chain polydispersity, which likewise appears responsible for enormous elongations (\textit{ca.} 4000\% strain) and enhanced fracture toughness.
Figure S3.1. Dependence of $T_m$ on OTPEG composition for the OBC15 (●) and OBC40 (○) series. The solid line serves as a guide for the eye.

Figure S3.2. Successive strain cycles measured from the OTPEG with 60 wt% OBC40. The maximum strain in each cycle is increased from 50 to 1000%.
References


4 Crystallization-Directed Anisotropic Electroactuation in Selectively-Solvated Olefinic Thermoplastic Elastomers: A Thermal and (Electro)Mechanical Property Study

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ABSTRACT

Dielectric elastomers (DEs), a class of soft electroactive polymers that change size upon exposure to an external electric field, constitute an increasingly important class of stimuli-responsive polymers due primarily to their large actuation strains, facile and low-cost fabrication, scalability, and mechanical robustness. Unless purposefully constrained, most DEs exhibit isotropic actuation wherein size changes are the same in all actuation directions. Previous studies of DEs containing oriented, stiff fibers have demonstrated, however, that anisotropic actuation along a designated direction is more energy efficient since this composite design eliminates wasted energy expended in non-essential directions. To identify an alternative, supramolecular-level route to anisotropic electroactuation, we investigate the thermal and mechanical properties of novel thermoplastic elastomer gels composed of a selectively-solvated olefinic block copolymer that not only microphase-separates but also crystallizes upon cooling from the solution state. While these materials possess remarkable mechanical attributes (e.g., giant strains in excess of 4000%), their ability to be strain-
conditioned enables huge actuation anisotropy levels, measured to be greater than 30 from the ratio of orthogonal actuation strains. This work establishes that crystallization-induced anisotropic actuation can be achieved with these DEs.
I. Introduction

While dielectric elastomer (DE) actuators were first discovered in the late 19th century by Röntgen,[1] broad interest in this stimuli-responsive class of electroactive transducers is relatively recent, flourishing over a century later.[2-5] Two primary reasons account for this sudden spike in technological interest: (1) development of flexible, stretchable and otherwise compliant electrode technologies, and (2) discovery of dielectric materials possessing the appropriate electrical and elastomeric properties required to attain large actuation strains. The seminal paper by Pelrine et al.[6] is largely responsible for spurring contemporary DE studies by introducing the use of carbon grease as a compliant electrode in conjunction with a new chemically-crosslinked dielectric material, a commercial acrylic adhesive (VHB 4905/4910), that is capable of achieving actuation strains greater than 100% (on an area basis). Since this initial investigation of VHB, the DE community has considered surprisingly few new competitive materials even though VHB remains somewhat proprietary and it is only manufactured in two thicknesses. Nevertheless, because of its performance, availability and relatively low cost, VHB has dominated the scientific literature as the gold standard to which the performance of other materials is frequently compared.[7-10] Other examples of chemically-crosslinked elastomers that have shown promise as DEs for use in, e.g., (micro)robotics,[11] biomedical devices[12] and stretchable electronics[13] include silicone elastomers,[14,15] VHB modified[16] with a secondary acrylic network to produce an elastomeric "binetwork," custom-designed acrylic elastomers,[17] and bottlebrush silicone elastomers. An important consideration in the use of such elastomers as DEs is the usual need to induce mechanical prestrain (to reduce specimen thickness and increase specimen modulus) prior to actuation. In
recent advances, prestrain can be locked-in\cite{16} or altogether eliminated\cite{18}.

Two additional design variations have likewise been reported. The first is the use of physically-crosslinked elastomers, such as block copolymers, to achieve giant actuation strains at lower electric fields than VHB\cite{19,23}. Block copolymers are macromolecules in which two or more contiguous sequences of chemically-dissimilar species are covalently attached\cite{24,25}. Because of the thermodynamic incompatibility between these sequences, the copolymers typically self-assemble and form soft nanoscale morphologies\cite{26,27} ranging from classical nanostructures (e.g., spheres, cylinders and lamellae) to more spatially complex ones (e.g., gyroid\cite{28,29}, $F_{dddd}$\cite{30,31} and truncated octahedra\cite{32}). Bicomponent triblock (as well as higher-order multiblock) copolymers consisting of glassy endblocks and a rubbery midblock are of noteworthy interest as thermoplastic elastomers\cite{33} (TPEs) in that they not only microphase-separate to form the same morphologies as their diblock analogs but also generate a molecular network\cite{34,35,36} wherein rubbery midblocks connect neighboring glassy microdomains (which act as physical crosslinks). Unlike their chemically-crosslinked counterparts, TPEs can thus be recycled and reused after their application lifetime. Incorporation of a midblock-selective oligomeric oil serves to either swell the rubbery network or induce a morphological transition\cite{32}. In the present case, midblock-swollen TPE gels (TPEGs) with tunable moduli and negligible strain-cycling hysteresis afford an alternative to VHB\cite{19,20}. While many TPEs are styrenic triblock copolymers\cite{37} and exhibit well-defined morphologies such as the one illustrated by Figure 4.1a, crystallizable block copolymers can adopt different variants depending on morphology-crystal interplay, as described by Loo et al\cite{38,39} and depicted in Figures 4.1b-d. In particular, some crystallizable TPEs possess polyolefin blocks\cite{40,41} and
yield TPEGs with intriguing mechanical properties.\textsuperscript{[43]}

The second design variation enables the anisotropic actuation of DEs. Insofar as DEs are not purposefully constrained to retain a given shape during actuation or fabricated in such fashion to promote direction-oriented actuation, amorphous DEs normally undergo isotropic actuation and change size equally in all actuating directions. Important details regarding the mechanism of DE actuation will be provided in a later section. If actuation is only required in a specific direction, energy is wasted if expended in all non-essential directions. To introduce anisotropic actuation into VHB-based DEs, several independent efforts\textsuperscript{[44-47]} have examined polymer composites prepared by incorporating aligned fibers into sandwiched VHB films. By doing so, the tensile moduli parallel and perpendicular to the fiber direction differ substantially, with the modulus along the fiber direction exceeding that normal to the fiber direction. As a consequence of this difference in mechanical properties, the electromechanical properties exemplified by the orthogonal actuation strains at a constant electric field display similar behavior. Mechanical and actuation anisotropy values can further be discerned\textsuperscript{[46]} from the ratios of these directional mechanical moduli and actuation strains, respectively, and yield actuation-induced enhancement factors (defined as the ratio of actuation to mechanical anisotropy) that vary linearly with fiber content and, in some cases, extend beyond 2.5x.\textsuperscript{[47]} Perhaps more importantly is the experimental result that anisotropic actuation serves to improve the electromechanical efficiency, which reflects the conversion from electrical input to mechanical output, by as much as 55%.\textsuperscript{[46]} While such composites depend on macroscopic anisotropy for anisotropic actuation, the primary objective of the present study is to promote microscopic anisotropy in olefinic TPEGs through the use of directional mechanically-
conditioned crystallization.

II. Results and Discussion

A. OBC considerations

The olefinic block copolymer (OBC) employed here belongs to a class of polymers synthesized by continuous chain-shuttling catalysis.\textsuperscript{[48]} According to prior studies,\textsuperscript{[40,41,49]} it consists of high-density polyethylene "hard" blocks and poly(ethylene-co-\(\alpha\)-octene) "soft" blocks. On the basis of its reported\textsuperscript{[50]} crystallinity (\(\approx 18\%\)), the hard block content is estimated to be 26 wt\%, and the corresponding molecular weight is about 121 kDa. Because of the chain-shuttling reaction, these TPEs possess a random multiblock architecture with polydisperse block lengths and block numbers. As a consequence of their long hard blocks, OBC TPEs typically possess superior thermal, mechanical and optical properties compared to elastomers based on olefinic random copolymers.\textsuperscript{[48]} In crystallizing block copolymers, the solid-state morphology is often templated by the melt morphology when the thermodynamic incompatibility (\(\chi N\), where \(\chi\) denotes the Flory-Huggins interaction parameter and \(N\) is the number of repeat units along the copolymer backbone) is sufficiently high to induce microphase separation (\textit{cf. Figure 4.1c}). At high incompatibility, microphase separation dominates and forces crystallization to remain confined within microdomain boundaries (\textit{cf. Figure 4.1b}).\textsuperscript{[39]} In addition to incompatibility, crystallization rate can play an important role in morphological development. For instance, rapid crystallization favors crystallization wherein incompatible segments cannot diffuse out of microdomains before being immobilized, thereby generating a so-called "breakout" morphology (\textit{cf. Figure 4.1d}).\textsuperscript{[39,51]} Due to the presence of highly ordered crystalline lamellae
in this morphology, numerous slip faces facilitate crystal reorganization under stress. In this case, this morphology displays "slip-link" behavior\cite{52} wherein physical crosslinks do not maintain permanent shape or location but instead slide along polymer chains upon deformation.

B. OTPEG crystallization

All the TPEGs examined here consist of the OBC swollen with an aliphatic white mineral oil, a soft-block selective solvent. These materials fundamentally differ from styrenic TPEGs\cite{8,19} and are therefore designated as OTPEG\textsubscript{x}, where \textit{x} refers to the mass fraction of OBC. This OTPEG series is chosen for study because of its mechanical properties (modulus and toughness) are ideal for effective DEs. Our previous investigation\cite{43} details some of the limitations of OTPEGs composed of OBCs with higher and lower crystallinities. Such limitations are attributed to insufficient midblock bridging, which at least partially reflects the chain/block polydispersity. Bridged soft blocks are crucial in the design of DEs since they comprise the network that connects semicrystalline microdomains and provides the elastic response required for a DE to relax after actuation cessation. The nature of these semicrystalline crosslinks likewise affects the mechanics of OTPEGs and can be altered by the crystallization rate. Quasistatic uniaxial tensile tests of OTPEG35 subjected to quench cooling (to 25°C) and isothermal crystallization (at 105°C) are compared in Figure 4.2a and immediately reveal that the quenched specimen attains a significantly greater tensile strength (maximum stress, \(\sigma\)) and extensibility (maximum strain, \(\varepsilon\)). The associated fracture energies of the quench-cooled and isothermally-crystallized OTPEGs are 21.5 ± 2.3 and 16.2 ± 2.6
MJ/m³, respectively, and corresponding polarized light microscopy (PLM) images of the specimens are presented in Figures 4.2b and 4.2c, respectively. In Figure 4.2b, slow nucleation yields large spherulites that measure up to 0.1 mm in diameter. Rapid isothermal crystallization of OTPEG80 between glass slides at ambient temperature proceeds on the order of seconds and results in radial growth rates of 5.71 ± 0.25 μm/s in Figure 4.3a. Similarly quick crystallization is likewise evident at lower OBC content (e.g., OTPEG60 in Figure 4.3b).

Thermograms acquired from differential scanning calorimetry (DSC) are provided in Figure 4.4a for the neat OBC and several OTPEGs varying in copolymer mass percent (w_{OBC}). While crystallization occurs too quickly to probe kinetics by DSC, the endotherm indicative of OBC melting is apparent in each thermogram in this figure and confirms that the peak melting temperature (T_m) systematically shifts to higher temperature with increasing w_{OBC}. This relationship, displayed over a broad composition range in Figure 4.4b, signifies that the thickness of the crystalline lamellae varies with w_{OBC} in accord with the Gibbs-Thompson equation:

\[
T_m = T_m^\infty \left(1 - \frac{2}{\Delta H_m} \frac{1}{d}\right)
\]

where \(T_m^\infty\) corresponds to \(T_m\) of a bulk specimen, \(\gamma\) is the interfacial energy, \(\rho\) is the mass density, \(\Delta H_m\) represents the heat of melting, and \(d\) is the lamellar thickness. For the present OTPEGs, \(T_m^\infty\) and the quantity \(2\gamma/(\rho\Delta H_m)\) are estimated\(^{[53]}\) as 140°C and 0.8 nm, respectively, so that \(d\) ranges from 8.9 at low \(w_{OBC}\) to 17.7 nm for the neat OBC. Another trend in Figure 4.4a is that the area under the endotherm (which relates to \(\Delta H_m\)) increases with increasing
w_{OBC}. Values of OTPEG crystallinity ($X_{c,g}$) calculated from the ratio $\Delta H_m/\Delta H_m^0$, where $\Delta H_m^0$ denotes the specific heat of melting for fully crystalline polyethylene (290 J/g from ref. 54), are included as a function of $w_{OBC}$ in Figure 4.4c and reveal the existence of a nearly linear relationship up to $\approx15\%$ for the neat OBC. By accounting for the composition of each OTPEG, the crystallinity of the OBC ($X_{c,p}$) can likewise be determined (cf. Figure 4.4c). In this case, relatively little variation in $X_{c,p}$ is observed from 20 to 100 wt% OBC. X-ray diffractometry of the OTPEGs yields the scattering profiles displayed in Figure 4.5. While these profiles are qualitatively consistent with the results from DSC, they suggest that the crystal lattice dimensions vary slightly with $w_{OBC}$ at 40 wt% OBC and below, but become independent of $w_{OBC}$ at 60 wt% OBC and above.

C. OTPEG mechanics

As with other families of TPEGs, the mechanical properties of OTPEGs are broadly tunable on the basis of composition, as evinced by the uniaxial tensile data provided in Figure 4.6a for OTPEGs with $w_{OBC}$ varied from 20 to 60 wt% OBC. As previously demonstrated for other OTPEGs, the extensibility increases substantially with increasing $w_{OBC}$ up to a point below 100 wt% OBC. Even at just 20 wt% OBC, the extensibility exceeds 2000% strain, whereas it more than doubles as it approaches 4200% strain at 60 wt% OBC. The extensibility of OTPEGs at less than 20 wt% OBC is severely limited due to low crosslink density. We propose that the practical limit for high extensibility of this OTPEG is about 15 wt% OBC, which corresponds to $\approx2.4\%$ gel crystallinity and $\approx15.7\%$ polymer crystallinity from Figure 4.4c (with a smaller fraction actively participating in network crosslinking). In addition, the
crystalline lamellar size is only about 10.6 nm (compared to 17.7 nm for the neat OBC). These correlations are consistent with a reduction in the number of elastomeric bridges due to a lower physical crosslink density. Various properties derived from uniaxial tensile data such as those presented in Figure 4.6a are included for comparison as functions of \( w_{\text{OBC}} \) in Figures 4.6b and 4.6c. Both the fracture energy, calculated from the area under each stress-strain curve analyzed, and the tensile strength are shown to increase exponentially with increasing \( w_{\text{OBC}} \) from 20 to 60 wt% OBC in Figure 4.6b. Over this composition range, the fracture energy is measured to increase by \( \approx 31 \times \) whereas the tensile strength increases by \( \approx 27 \times \). In Figure 4.6c, the tensile (or Young's) modulus (\( Y \)) likewise is observed to increase (exponentially) by as much as 30\( \times \) with increasing \( w_{\text{OBC}} \). As discussed in the next section, the modulus plays a generally important role in DE electroactuation, and the results provided in Figure 4.6c confirm that the tensile modulus of OTPEGs is composition-tunable.

Although the tensile measurements portrayed in Figure 4.6 render valuable insight into the mechanical properties of OTPEGs, we examine their dynamic shear behavior in this section to ascertain whether they exhibit the rheological properties expected of network systems. The dynamic storage modulus (\( G' \)) affords a measure of the solid-like properties of relatively soft materials, such as polymers or colloids. All the frequency (\( \omega \)) spectra for \( G' \) displayed in Figure 4.7a have been acquired in the linear viscoelastic regime in which both \( G' \) and the dynamic loss modulus (\( G'' \)) are independent of strain amplitude and therefore representative of the material being measured. Two important features are evident in Figure 4.7a. The first is that, in agreement with the measured values of \( Y \) in Figure 4.6c, \( G' \) increases monotonically with increasing \( w_{\text{OBC}} \). Values of \( G' \) averaged over the low- \( \omega \) regime from 0.1 to 1.0 rad/s are
included for comparison with Y in Figure 4.6c and are generally lower than Y. According to these results, the ratio of Y/G’ varies from ≈6.4 at 50-60 wt% OBC to ≈1.8 at 30-40 wt% OBC. At 20 wt% OBC, G’ ≈ Y. Another aspect of Figure 4.7a is that G’ is generally independent of ω insofar as wOBC exceeds a specific value. This is more clearly seen in Figure 4.7b, wherein tan δ (= G''/G’) is presented as a function of ω. If both G’ and G” are independent of ω, then so will tan δ, which constitutes the basis of the Winter-Chambon criterion[55] for network rheology. When tan δ depends on ω, however, the system no longer possesses a network according to this criterion and consists of flocs. In Figure 4.7b, the copolymer network appears to be compromised between 7.5 and 10.0 wt% OBC, which is consistent with our earlier deduction (that an optimal composition is about 15 wt% OBC) proposed on the basis of thermal and mechanical properties.

D. OTPEG electroactuation

1. Isotropic DEs

For a DE to be successful, the mechanical and electrical properties of an elastomer must be balanced. The mechanism by which DEs undergo electroactuation is illustrated in Figure 4.8. When an electric field (E = Φ/H, where Φ represents the potential and H is the thickness of the elastomer film) is applied to a DE that has been coated on both sides with compliant electrodes, a compressive Maxwell stress (σM) develops normal to the film surface. The magnitude of the Maxwell stress for an ideal DE is written as[6]

\[ σ_M = \varepsilon_0 E^2 \]  

(2)
where $\varepsilon'$ is the relative dielectric permittivity (the dielectric constant) of the elastomer, and $\varepsilon_0$ is the dielectric permittivity of vacuum. In most cases, $E$ is taken as the nominal electric field relative to the initial film thickness ($H_0$). For the present nonpolar OTPEGs, $\varepsilon'$ is not strongly dependent on $w_{OBC}$ or $\omega$, averaging just under 2.0, which means that the DE must be very soft to achieve sizable actuation. For this reason, only OTPEGs at low $w_{OBC}$ (< 30 wt% OBC) are considered further as DE candidates. Moreover, since the improved toughness and extensibility of quench-cooled OTPEGs suggests that they will perform better as DEs than their isothermally-crystallized analogs, the OTPEGs employed in this section will be quench-cooled at 25°C. In response to the attraction of the oppositely-charged electrodes and the accumulation of like charges along each electrode upon actuation, the elastomer film depicted in Figure 4.8 thins in the transverse ($z$) direction and isotropically expands in the lateral ($x$ and $y$) directions. Since this process is isochoric, expansion in the lateral directions is directly related to the thickness change along the transverse direction. In the Hookean limit, the transverse strain ($s_z$) is given by

$$s_z = \varepsilon_0 E^2 / Y$$  \hspace{1cm} (2)

The first step to decide whether the present OTPEGs can serve as satisfactory DEs is to subject them to isotropic electroactuation and compare their actuation performance with other elastomers.\cite{7-10} Since these OTPEGs display little evidence of strain stiffening during tensile deformation (cf. Figure 4.6a), they constitute poor choices for prestrain-free actuation, in which case films (measuring 1 mm thick) of OTPEG15 and OTPEG20 are first fixed to conventional circular test frames and then equibiaxially prestrained to 100% x 100% prior to actuation. Higher prestrain values are not considered since OTPEG15 undergoes mechanical
failure. Results from actuation tests are presented in Figure 4.9a and reveal that the maximum actuation strains are 31 and 11% for OTPEG15 and OTPEG20, respectively. While these OTPEGs possess moduli that are comparable to other high-strain DEs, their actuation performance is disappointingly inferior. For example, two styrenic TPEGs of identical composition, thickness and prestrain are included in Figure 4.9a for comparison. To elucidate the reason for such limited OTPEG performance, we have conducted a stability analysis on the basis of the pioneering works of Suo. In this analysis, the nominal electric field is examined as a function of the actuation expansion ratio \( \lambda = L/L_0 \), where \( L_0 \) and \( L \) correspond to the specimen length before and after actuation) according to

\[
E(\lambda) = \frac{2}{z} \sqrt{\frac{(\lambda)}{0}}
\]

The stability of a DE requires that \( E \) (and, hence, \( \Phi \) at constant \( H_0 \)) increases monotonically as a function of \( \lambda \) so that \( dE/d\lambda > 0 \). Existence of an inflection point introduces an electromechanical, commonly referred to as a "snap-through," instability, which identifies the isofield condition when \( \sigma_M \) exceeds the mechanical resistance of the DE. This instability is survived or suppressed due to strain stiffening for DEs capable of large actuation strains. Failure of a DE can alternatively be caused by dielectric breakdown at the condition where \( E_B = E*/\lambda^2 \). Here, we have used 24-32 kV/mm as the range for \( E* \) on the basis of dielectric strength measurements. Whereas OTPEG20 fails near the upper limit of \( E_B \) in Figure 4.9b, OTPEG15 most likely fails before reaching the lower limit of \( E_B \) due to mechanical limitations rather than dielectric failure.

Inclusion of actuation data from the styrenic TPEGs in Figure 4.9 helps to elucidate several
differences in (electro)mechanical behavior with regard to the OTPEGs. First, both styrenic TPEGs not only achieve significantly higher actuation strains (in one case over 90%) than either OTPEG but also exhibit non-monotonic behavior that is indicative of an electromechanical instability. While such instability is evident in each of the datasets shown in Figure 4.9b, neither styrenic TPEG survives/suppresses the instability to reach much larger actuation strains. At higher prestrain values, however, it is reasonable to presume that these styrenic TPEGs likely survive or completely suppress the instability during electroactuation to achieve giant actuation strains (that, in fact, approach 300%).[58] In comparison, the OTPEGs never reach the point of instability before dielectric breakdown occurs and, for this reason, cannot match the DE performance of the styrenic TPEGs. This shortcoming is directly attributable to the plastic deformation and high strain set encountered with OTPEGs due to their semicrystalline nature and multiblock architecture. Sufficient strain stiffening necessary to ensure instability suppression does not occur in OTPEGs during their first strain cycle. By identifying the reason for relatively poor electroactuation performance, however, we next introduce a mechanical conditioning approach to overcome this limitation and, in the process, produce OTPEG-type DE actuators that operate without mechanical prestrain and concurrently impart sufficient strain stiffening to suppress the electromechanical instability and achieve anisotropic electroactuation.

2. Anisotropic DEs

Dielectric elastomers are generally produced from mechanically isotropic elastomers since the nanoscale crosslinks responsible for network stability are, on average, randomly oriented
and uniformly spaced. As a result, the strain response to an applied stress is the same regardless of the applied stress direction. In the present scenario, this means that, when an external electric field is applied to an isotropic DE, the elastomer is transversely compressed and expands uniformly in lateral directions, as illustrated in Figures 4.8 and 4.10. Due to the isochoric nature of the deformation, the transverse and lateral actuation expansion ratios are related through

\[ 2 \lambda_x(1 - \nu) = \frac{1}{\lambda_x \lambda_y} \]  

where the subscripts indicate the strain directions according to the coordinates in Figure 4.8, and \( \nu \) is Poisson’s ratio. Since elastomers are routinely presumed to be incompressible with a Poisson’s ratio of \( \approx 0.5 \), we use this limiting value to obtain a general expression applicable for elastomers, i.e., \( \lambda_x \lambda_y \lambda_z = 1 \). In the specific case of isotropic deformation or actuation, \( \lambda_x = \lambda_y = \lambda \) so that \( \lambda^2 \lambda_z = 1 \). These two compressive deformation conditions — isotropic and anisotropic — are depicted in Figure 4.10. Introduction of anisotropy into DEs is particularly important for bimorph actuators and artificial muscle and has been previously achieved through directional prestraining of elastomers that would normally undergo isotropic electroactuation. In this situation, anisotropic actuation is the result of the process by which actuation is conducted and not by the DE. An alternative approach relies on material modification to achieve anisotropic actuation. As mentioned earlier, one strategy focuses on the fabrication of composite DEs into which aligned fibers are inserted (cf. Figure 4.11a), whereas another recent methodology enables anisotropic actuation through the use of oriented carbon nanotubes comprising the compliant electrodes.
Because of the semicrystalline crosslinked network that exhibits slip-link behavior in OTPEGs, mechanical anisotropy can be introduced into OTPEGs by straightforward uniaxial strain cycling. The result is a compositionally-unaltered DE endowed with microscopic anisotropy. We hereafter refer to this strain-induced rearrangement of crosslinks, depicted in Figure 4.11b for comparison with fiber composites, as mechanical conditioning. By taking advantage of the general tunability of OTPEGs, the degree of crosslink alignment and the resulting anisotropic (electro)mechanical properties can be tailored for a particular application via several material-related factors: the composition and molecular weight/architecture of the OBC (which are constant in this study), the concentration of OBC in the OTPEG (w_{OBC}), and the extent of conditioning. For proof-of-concept purposes, the copolymer concentration is held constant at 25 wt% OBC, which provides sufficient toughness and stiffness for strain cycling and actuation, respectively, and is higher than the ones discussed with regard to isotropic actuation in Figure 4.9. The last consideration mentioned above is examined in Figure 4.12, which displays true stress as a function of tensile strain for OTPEG25 after strain cycling in pure shear mode (i.e., \( \lambda_x = 1/\lambda, \lambda_y = 1 \) and \( \lambda_z = \lambda \)) to three different strain levels (in \%) : 1000, 1500 and 2000. Note that strains up to 2000\% are not purely shear (but a combination of shear and tension) due to the impractical size of the specimen required. Although the results displayed in Figure 4.12 reveal that the initial cycle to 2000\% strain is accompanied by significant hysteresis after plastic deformation, specimens subjected to mechanical conditioning for 5 cycles to each of the three strain levels at a high strain rate (10\%/s) show much less evidence of hysteresis with unrecoverable, or set, strain values of 270\% (1000\%), 420\% (1500\%) and 540\% (2000\%).
After mechanical conditioning, these OTPEG25 specimens exhibit unequivocal evidence of mechanical anisotropy (defined as the ratio of the parallel modulus to perpendicular modulus in relation to the strain direction): 1.3 (1000%), 2.9 (1500%) and 1.6 (2000%). While the maximum anisotropy is observed after strain cycling to 1500%, the underlying reason responsible for this result is not completely understood at the present time, although we posit that it might reflect the tensile contribution and associated material damage at 2000% strain. In any case, electroactuation is anticipated to follow the mechanical anisotropy. Linear actuation strains measured along orthogonal directions for each of the mechanically-conditioned OTPEG25 specimens with no mechanical prestrain are provided as functions of E in Figure 4.13a and confirm that the specimens strain-cycled to 1500 and 2000% actuate anisotropically. Actuation strains perpendicular to the conditioning direction are higher than those of softer equibiaxially prestrained OTPEGs (cf. Figure 4.9). This observation is an important result that allows for the design of an anisotropic, prestrain-free DE capable of outperforming its isotropic, prestrained counterpart. Relative to other prestrain-free DEs, mechanically-conditioned OTPEGs attain higher linear actuation strains (16%) than styrenic TPEGs (9%) and VHB (4%). Corresponding values of the actuation anisotropy calculated from the orthogonal actuation strains in similar fashion as the mechanical anisotropy are included in Figure 4.13b and reveal several interesting outcomes. The first is that strain-cycling OTPEG25 to 1000% has no discernible effect on anisotropic actuation, whereas OTPEG25 mechanically conditioned at 1500% achieves the highest anisotropy (> 30) of the series. As expected on the basis of mechanical anisotropy, the specimen conditioned at 2000% undergoes less, but not negligible (> 2), anisotropic actuation.
For comparison in Figure 4.13b, results acquired\textsuperscript{[46]} from a VHB-4905 DE equibiaxially prestrained to 200% x 200% and modified with unstrained polyurethane (PU) fibers displays actuation anisotropy levels that are generally < 2. Also included in Figure 4.13b are the highest reported\textsuperscript{[47]} values of composite DEs composed of prestrained VHB-4905 and containing one of the following fibers: PU (strained to 200%), polyamide (PA) and silicon carbide (SiC). This comparison confirms that the supramolecular approach introduced here to align the semicrystalline crosslinks via mechanical conditioning is on par with or superior to methods intended to achieve anisotropic actuation through the incorporation of aligned fibrous modifiers. Another advantage of the present strategy is that DEs derived from conditioned OTPEGs can be fabricated to be very thin (on the order of tens of micrometers) due to their inherent toughness. This consequently brings the actuating voltage down to the sub-kilovolt range. Lastly, prior to failure by dielectric breakdown, conditioned OTPEGs experience a loss of tension and form wrinkles parallel to the direction of conditioning. While the periodicity of the wrinkles appears to be related to film thickness, further investigation of this phenomenon is clearly warranted to establish whether a meaningful relationship in fact exists. In this spirit, however, several studies\textsuperscript{[60,61]} have independently confirmed that the periodicity of wrinkles in polymeric films is governed by material attributes such as the modulus.

3. Instability suppression

Mechanical conditioning of crystallizable DEs undoubtedly constitutes a facile route by which to fabricate DEs for applications requiring anisotropic (linear) actuation. Another subtle, but important, benefit of strain cycling OTPEGs is the occurrence of a substantial Mullins
effect\textsuperscript{[62]} that is commonly encountered in filled rubber. This effect refers to material softening when an elastomer exceeds the maximum strain previously reached. The relevance of this effect is visible in the final 20-30\% of the stress-strain curve (\textit{cf. Figure 4.12}) as the OTPEG approaches the prior maximum strain. In this strain range, the OTPEG with relatively poor strain-stiffening behavior during its first strain cycle is softened and develops much improved strain stiffening upon subsequent strain cycles, which helps to explain why we elected to use 5 cycles in our electroactuation measurements. Although common DEs possessing ideal electromechanical properties such as low cyclic hysteresis, instability suppression, high extensibility, and low modulus do not benefit significantly from the Mullins effect, the strain-stiffening response of mechanically-conditioned OTPEGs can be tailored to eliminate electromechanical instabilities. A similar approach has been reported\textsuperscript{[63]} for DEs composed of filled rubber. To explore the applicability of this effect on the electroactuation of conditioned OTPEGs, we have incorporated the stress-strain curves generated from mechanical conditioning of OTPEG25 at different strain levels into Eq. 1 to predict the electric field (at a constant film thickness of 1 mm) required for actuation. The results presented in Figure 4.14a confirm that conditioning at higher strain levels reduces the potential required for actuation and improves the likelihood of surviving the snap-through instability and reaching higher actuation strains.

At a conditioning strain of 1500\%, for instance, modest actuation strain (\approx 27\%) is expected from OTPEG25 before failure by dielectric breakdown occurs (at $\lambda = 1.26$). Increasing the conditioning strain to 2000\% extends the plateau region prior to strain stiffening and ultimately induces a snap-through instability (at $\lambda = 1.38$) that continues until mechanical failure or
dielectric breakdown. An actuation curve predicted from the first strain cycle (without subsequent conditioning) is displayed in Figure 4.14a to demonstrate that snap-through occurs (at $\lambda = 1.36$) with no instability suppression whatsoever. Unfortunately, the snap-through point is well beyond the breakdown field at a predicted strain of $< 2\%$. This example illustrates the major complication associated with these predictions, namely, most of the beneficial electromechanical behavior occurs beyond the breakdown field of OTPEGs. Mechanical conditioning over the range of 1600-1800\% appears to be optimal for preventing instability while allowing for reasonably large actuation strains. Experimental data included in Figure 4.14a for OTPEG25 conditioned at 1200 ± 200\% strain lie between the predicted curves corresponding to 1000 and 1500\% conditioning, as expected. This DE fails due to dielectric breakdown near the predicted breakdown curve. Electroactuation of this conditioned OTPEG is performed with a diaphragm actuator that is inflated at 13 kPa to condition the actuator and then stimulated at 0.5 kPa. An intriguing feature not previously reported for DEs to the best of our knowledge is displayed in Figure 4.14b: the active area coated with the compliant electrode (dark) stretches the surrounding material during actuation. This unexpected result presents an excellent opportunity to study the mechanical interplay and stress transfer between actuating and non-actuating regions of DEs. In addition, the mechanics-based predictions in Figure 4.14a provide a basis for a viable strategy to overcome the electromechanical instability of crystallizable DEs by mechanical conditioning.

III. Conclusions

Thermoplastic elastomer gels composed of olefinic multiblock copolymers constitute a
unique class of crystallizable soft materials in that their properties can be tuned through not only copolymer attributes\textsuperscript{[43]} (e.g., molecular composition, weight and architecture, as well as gel concentration) but also crystallization rate and mechanical conditioning. In this regard, these materials differ from conventional TPEGs and facilitate access to unusual (electro)mechanical properties. In this work, we have investigated the thermomechanical properties of OTPEGs generated from a single copolymer and demonstrated that crystallization of the crosslinks responsible for network stabilization occurs quickly. The melting point and gel crystallinity are measured to increase systematically with increasing copolymer content. Various mechanical properties derived from uniaxial tensile tests reveal broad tunability of extensibility (beyond 4000\% strain), tensile strength, fracture energy, and moduli. Complementary dynamic rheological analysis confirms the existence of a sol→gel transition below 10 wt\% copolymer. These properties are employed to design mechanically-prestrained DEs, which do not actuate isotropically as well as styrenic TPEGs and other common elastomers due presumably to the absence of an snap-through instability before reaching dielectric breakdown.

Through isothermal mechanical conditioning, however, we have discovered that these DEs can be endowed with microscopic anisotropy attributable to the development of oriented semicrystalline crosslinks. These OTPEG-based DEs actuate with no mechanical prestrain and high anisotropy, reaching relatively large linear actuation strains up to 16\%. While the combination of mechanical conditioning in conjunction with a semicrystalline elastomer to introduce plastic deformation and anisotropic (electro)mechanical properties is important, we recognize that the particular material employed here might not necessarily be the best choice
to fabricate products of immediate commercial interest. Other semicrystalline elastomers with superior electrical properties (e.g., dielectric constant and/or breakdown strength) have the potential for exceptionally better performance than the OTPEGs examined here by reducing the operating voltage and, more importantly, suppressing the electromechanical instability to survive to much larger actuation strains. Our results reported herein nonetheless establish the promising and, in some case, remarkable properties of OTPEGs and introduce a novel strategy by which crystallizable elastomers can readily access anisotropic actuation without relying on confinement effects during fabrication or the incorporation of anisotropic additives.

IV. Experimental

The OBC used in this study (Infuse 9100) was kindly provided by the Dow Chemical Co. in pellet form with no additives (specifically talc, which is often used to reduce pellet adhesion). The soft-block-selective diluent was the same aliphatic white mineral oil (Hydrobrite 380, Sonneborn) employed in earlier studies of styrenic TPEGs. Semi-permanent strong physical gels were formulated by solvent-assisted melt mixing. Polymer pellets were hand-mixed with mineral oil in predetermined mass fractions for each w_{OBC} value and then dissolved at a concentration of 5% w/w or lower in xylene at 120°C for 0.5-2.0 h. The OTPEGs crystallized rapidly upon cooling and were dried at ambient temperature for at least 7 d, after which they were annealed for 8-12 h under vacuum at 130°C to remove residual xylene. The PLM images were collected on a Nikon Optiphoto microscope, and the DSC thermograms were measured with a TA Q20 calorimeter at a constant heating rate of 10°C/min. X-ray diffractometry was conducted on beam line 12-ID-B at the Advanced Photon Source
(Argonne National Laboratory) in accord with the experimental details provided elsewhere,\cite{64} and resultant 2D data were collapsed down to 1D intensity profiles as a function of the scattering vector (q). Quasistatic uniaxial tensile tests and mechanical conditioning were performed at ambient temperature on an Instron load frame (Model 5943) operated at a strain rate of 10%/s. The dielectric constants of OTPEG films outfitted with circular copper electrodes were measured with a handheld Fluke 117 True RMS multimeter at 1 kHz. Unless otherwise indicated, electroactuation was performed on a circular test frame with an Agilent 33220A arbitrary waveform generator amplified by a Trek 609E-6 voltage amplifier. Digital images collected with a DSLR camera were analyzed with ImageJ. Diaphragm actuation tests were conducted in a 30 mm x 30 mm x 40 mm airtight acrylic pressure vessel. The elastomer film was attached across the top surface of the vessel, and the pressure needed to promote directional inflation during actuation was precisely regulated.\cite{18}

V. Acknowledgments

The authors are grateful to Becton Dickinson Technologies, the Eastman Center of Excellence and DFG Grant EXC 1027 Bild Wissen Gestaltung for financial support, and we thank Dr. K. E. Mineart (Bucknell University) and Dr. B. Lee (Argonne National Laboratory) for technical assistance. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.
VI. References


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   *Proc. of SPIE Electroactive Polymer Actuators and Devices (EAPAD) XIX 2017.*

VII. List of Figure Captions

**Figure 4.1.** Schematic illustration of crystallizable block copolymer morphologies proposed by Loo *et al.*[^38,39] (a) melt, (b) confined, (c) templated, and (d) breakout.

**Figure 4.2.** In (a), quasistatic uniaxial tensile behavior of OTPEG35 after either quench cooling to 25°C or isothermal crystallization at 105°C (labeled). A pair of PLM images corresponding to these crystallization conditions are included in (b) and (c), respectively.

**Figure 4.3.** PLM images acquired from (a) OTPEG80 and (b) OTPEG60 at different times (labeled) to indicate the time scale over which crystallization occurs in these materials.

**Figure 4.4.** In (a), DSC thermograms measured from four OTPEGs varying in OBC content (w_{OBC}, labeled). Values of the peak melting point (T_m) extracted from calorimetry are presented as a function of w_{OBC} in (b). Included in (c) are gel (□) and polymer (■) crystallinities derived from melting endotherms such as those visible in (a). The solid lines in (b) and (c) serve as guides for the eye, and the dashed line in (b) corresponds to the crystallinity of the neat OBC.

**Figure 4.5.** X-ray diffraction intensity profiles presented as a function of the scattering vector (q) and acquired at ambient temperature from OTPEGs systematically varying in w_{OBC} (in wt%) from top to bottom: 100, 80, 60, 40, 20, 15, 10, and 5.

**Figure 4.6.** In (a), uniaxial tensile results from OTPEGs varying in w_{OBC} (labeled). Values of the fracture energy (◯) and tensile strength (●) extracted from stress-strain curves measured at ambient temperature are provided as functions of w_{OBC} in (b), whereas corresponding tensile moduli (Y, ◯) and dynamic storage shear moduli (G', ●) are included in (c). The solid lines in (b) and (c) are exponential regressions to the data and serve as guides for the eye.

**Figure 4.7.** Values of (a) G' and (b) tan δ displayed as functions of frequency (ω) at ambient
temperature for OTPEGs varying in wOBC (in wt%): 3.0 (■), 5.0 (□), 7.5 (●), 10.0 (○), 20.0 (▲), 30.0 (▲), 40.0 (◆), 50.0 (◇), and 60.0 (×). Solid lines serve to connect the data.

**Figure 4.8.** Illustration of the operational mechanism of a DE.⁶ Upon application of an electric field, a Maxwell stress develops perpendicular to the film to compress the DE transversely (along z) and concurrently promote lateral expansion (along x and y in Cartesian coordinates).

**Figure 4.9.** In (a), isotropic electroactuation results presented for OTPEG15 (○) and OTPEG20 (▲) at ambient temperature. Included are data for comparable TPEGs derived from a poly[styrene-\(b\)-(ethylene-co-butylene)-\(b\)-styrene] (SEBS) triblock copolymer at identical copolymer loading levels (in wt%): 15 (●) and 20 (▲). In (b), the same data are replotted for a stability analysis to identify the mechanism of DE failure. The solid lines are guides for the eye, and the shaded region in (b) identifies the range of dielectric breakdown discussed in the text.

**Figure 4.10.** Schematic diagram depicting the idealized difference between isotropic (top) and anisotropic (bottom) electroactuation.

**Figure 4.11.** Illustration of anisotropic electroactuation achieved in (a) fiber composites and (b) crystallizable TPEGs. The high-modulus direction lies along the fiber or conditioning direction.

**Figure 4.12.** Uniaxial tensile behavior of OTPEG25 under several strain conditions. The initial strain cycle reveals considerable hysteresis (solid line). The remaining data correspond to mechanical conditioning wherein the OTPEG is strain-cycled 5 times (in primarily shear mode) at three different strain levels (in %): 1000 (▲), 1500 (○) and 2000 (□).
**Figure 4.13.** Linear actuation strains (a) and actuation anisotropy (b) provided for prestrain-free OTPEG25 after the mechanical conditioning regimens shown in Figure 4.12. In (a), the conditioning strain levels (in %) are 1000 (triangle), 1500 (circle) and 2000 (square), and the open and filled symbols identify actuation strains perpendicular and parallel, respectively, to the conditioning direction (cf. Figure 4.11). In (b), the actuation anisotropy discerned from the ratio of orthogonal strains is presented for OTPEG25, as well as a polymer composite\[46\] consisting of equibiaxially prestrained VHB-4905 acrylic elastomer containing aligned, unstrained PU fibers (◆). Maximum anisotropies achieved with other fiber-modified VHB-4905 composites (labeled) are included for comparison.\[47\] The solid lines in (a) and (b) serve as guides for the eye.

**Figure 4.14.** In (a), electroactuation curves predicted from Eq. 1 on the basis of the mechanical conditioning regimens in Figure 4.12: first cycle (solid line), 1000% (△), 1500% (○), and 2000% (□). The dashed line identifies the onset of dielectric breakdown, and experimental data are included for OTPEG25 mechanically conditioned at 1200% (●). In (b), a photograph of OTPEG25 during isotropic actuation in a diaphragm testing frame as it approaches its dielectric breakdown. The dark coating corresponds to the compliant electrode.
Figure 4.1.

(a)  (b)  (c)  (d)

Figure 4.2.

(a)  

(b)  (c)  

Nominal stress, $\sigma$ (MPa)  

Tensile strain, $\varepsilon$ (%)  

Quenched  

Isothermally crystallized  

50 $\mu$m
Figure 4.3.
Figure 4.4.
Figure 4.5.
Figure 4.6.
Figure 4.7.
Figure 4.8.
Figure 4.9.
Figure 4.10.
Figure 4.11.

Figure 4.12.
Figure 4.13.
Figure 4.14.
5 Bottlebrush elastomers: A new platform for freestanding electroactuation

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Pre-straining elastic networks remarkably enhances actuator stroke in dielectric elastomers (DEs), making them the leading technology for artificial-muscle applications. However, external pre-strain protocols severely limit both actuator performance and device implementation. This drawback persists with only minimal advances in actuation of single-component elastomers realized since the dawn of the “pre-strain era” introduced by Pelrine et al. (2000). Now we present a molecular-based platform for the design of freestanding DEs derived from bottlebrush polymers. This architecture features inherently strained polymer networks that can be readily adapted to a variety of chemistries. To validate this concept, we have synthesized bottlebrush silicone elastomers that undergo giant electroactuations (>300%) at relatively low fields (<10 V m⁻¹) in as-cast shapes. These materials outperform all commercial DEs to date and open new opportunities in soft-matter robotics.

The pursuit of high performance artificial muscles has been greatly bolstered by the introduction of dielectric elastomers (DEs)¹⁻⁷ that readily undergo sizable (>100%), rapid (>1 kHz), and reversible deformation in response to an electric field.⁸⁻¹¹ These unique attributes,

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This chapter is a concatenation of a communication which has been published in Advanced Materials (Adv. Mater. 2017, 29, 1604209) and the supplemental information to that paper.
however, are impeded by premature breakdown due to electromechanical instability,\textsuperscript{12} which can be visualized using the simplest actuator configuration - a DE film sandwiched between two compliant electrodes (Fig. 1A). The transverse contraction $\lambda = d/d_0$ is governed by the mechanical properties of the film through a relationship between the applied voltage $\Phi$ and the resultant stress $\sigma(\lambda)$ given by $\Phi \sim \lambda \sqrt{\sigma(\lambda)}$.\textsuperscript{13} For conventional elastomers composed of flexible strands and exhibiting a strain-independent modulus (line 1 in Fig. 1B), this relationship displays a maximum in areal expansion at $\lambda^{EMI}_{\phi} \equiv \lambda^{-1} \approx 1.59$ (line 1 in Fig. 1C), which designates the onset of an electromechanical instability (EMI) \textsuperscript{(13)}. In voltage-controlled operation, the EMI generates an abrupt reduction in film thickness, which is typically followed by electrical breakdown, as indicated by the dashed arrow in Fig. 1C. As discussed previously,\textsuperscript{13} pre-stretching a DE by either fastening to a rigid frame,\textsuperscript{8} introducing an interpenetrating polymer network,\textsuperscript{14} solvent swelling\textsuperscript{15,16} and pressure modulation,\textsuperscript{17} or lamination promotes rapid onset of strain-stiffening which prevents EMI. However the above methods lead to increased device weight and size (rigid frames), decreased DE flexibility (interpenetrating networks), solvent leakage on actuation (swelling), and interfacial failure (lamination). The challenge is therefore to develop a single-component material that inherently undergoes strain-stiffening so that it does not require any type of pre-actuation manipulation. Moreover, designing elastomers possessing both low modulus and high extensibility enables large stroke and low-voltage operation required for biomedical applications.\textsuperscript{18-21} Finally, we desire to tune both stiffness and elasticity over a broad range without altering network chemistry or incorporation of a second component, such as a polymer, solvent, or filler.
Such inherently pre-strained, single-component elastomers can be created by introducing multiple, covalently-linked side chains along the network strands, yielding so-called bottlebrush networks composed of extended strands and possessing low Young's moduli (line 3 in Figure 5.1B). An important consideration in the molecular design of DEs is that the polymer chains in bottlebrush elastomers are disentangled (fig. S1), which releases the molecular constraint on high extensibility. This unique combination of mechanical properties – inherent strain-stiffening, low modulus, and high elasticity – affords controllable electroactuation of thick, freestanding DE samples over a broad range of strains at low voltages. Figure 5.2 shows two characteristic examples of such actuators: (i) a deflecting diaphragm and (ii) an elongating tube. In the first case (Fig. 2A), an as-cast PDMS bottlebrush elastomer film undergoes over 4× areal expansion prior to electrical breakdown (movie S1). In the second example (Fig. 2B), a tube of identical elastomer displays reversible elongation and dilation (movie S2). In the diaphragm configuration, we have achieved an unprecedented areal strain $\varepsilon_a \cong 300\%$, greatly exceeding the 120% benchmark reported for pre-strained (280%) silicone elastomers and compares favorably with the 380% actuation of a binetwork acrylic elastomer. Furthermore, the actuating diaphragm can lift a ball 30× heavier than the actuator, displaying an excellent payload to mass ratio. The tube sample also displays high performance, comparable to so-called spring-roll actuators, achieving 25% stroke. These remarkable results are particularly noteworthy as they were achieved for freestanding, as-cast shapes subjected to neither mechanical nor chemical modification.
Elimination of polymer chain entanglements in bottlebrush systems allows tuning bulk mechanical properties over a remarkably broad range without changing chemical composition. By independently varying the side-chain length, grafting density and crosslink density, we can synthesize DEs with Young’s moduli ranging from 1 MPa down to ~100 Pa and elongations at break up to ~10^{24}. In light of the unique properties achievable with bottlebrush elastomers, we first outline the basic principles of architectural control over mechanical properties. For a broad class of unentangled polymer networks, it has been demonstrated\textsuperscript{25} that the stress-strain relation can be expressed in universal form as

$$\sigma_{\text{true}}(\lambda) = \frac{G}{3}(\lambda^2 - \lambda^{-1}) \left[ 1 + 2 \left( 1 - \frac{\beta I_1(\lambda)}{3} \right)^2 \right]$$  \hspace{1cm} (1)

where $I_1(\lambda) = \lambda^2 + 2/\lambda$ corresponds to the first invariant for uniaxial network deformation at a constant volume. Thus, the elasticity of a bottlebrush network is effectively described by two molecular parameters – (i) the structural shear modulus ($G \approx \rho k_B T / n_s$) characterized by the number of monomeric units in the network strand $n_s \approx n_x (n_{sc} + 1) / n_g$, and (ii) the strand elongation ratio at rest ($\beta = \langle R_{\text{in}}^2 / R_{\text{max}}^2 \rangle$) defined as the ratio of the mean square end-to-end distance of a network strand in the initial (as-prepared) elastomer and the square of the length of a fully extended strand. Here, $\rho$ - monomer number density, $k_B$ - Boltzmann constant, and $T$ - absolute temperature. It is important to recognize that this parameter $\beta$ controls the strain-stiffening behavior required for the stable electroactuation. Unlike linear-chain systems ($n_{sc} = 0$), for which $G$ and $\beta$ simultaneously depend on crosslink density as $\sim n_x^{-1}$, bottlebrush elastomers allow for orthogonal control of modulus and extensibility through variation of the backbone fraction $n_g / n_{sc}$ as (24)
\[ G = C_1 \frac{\rho k_B T}{n_x (n_{sc}/n_g + 1)} \sim \frac{n_g}{n_{sc}} n_x^{-1} \]  \tag{2}

\[ \beta = C_2 \left( \frac{n_{sc}}{n_g} + 1 \right)^{1/2} n_x^{-1} \approx \frac{n_{sc}}{n_g} n_x^{-1} \]  \tag{3}

where \( C_1 \) and \( C_2 \) are numerical prefactors on the order of unity (0.3 and 3.1 obtained for our systems in Fig. 3B) that account for specific network compositions. From Eqs. 2 and 3, we can draw several important conclusions relevant to the performance of DE actuators. First, bottlebrush networks are softer than their entangled linear-chain counterparts, which allows for larger actuator stroke at lower voltages. Second, the additional architecture parameter \( \phi = n_g/n_{sc} \) (molar fraction of the bottlebrush backbone) allows for simultaneous reduction of the modulus \( (G \sim \phi) \) and enhancement of strain-stiffening \( (\beta \sim \phi^{-1/2}) \), which provides an unexplored molecular-level approach for tuning DE elasticity. Third, independent synthetic control of \( n_x, n_{sc}, \) and \( n_g \) permits variation of DE mechanical properties over much broader and previously inaccessible ranges as demonstrated below.

Two series of bottlebrush elastomers with poly(dimethylsiloxane) (PDMS) side chains possessing \( n_{sc} = 14 \) and 28 have been prepared by photo-initiated radical polymerization of monofunctional macromonomers in the presence of difunctional crosslinkers (fig. S2). All molecular characteristics are summarized in Table 5.1. Unlike previously reported synthetic strategies,\(^{26}\) the method developed here allows one-step preparation of different macroscopic shapes at gel fractions of 91±4\%. Figure 5.3A displays stress-strain curves measured upon uniaxial extension of PDMS bottlebrush elastomers with \( n_{sc} = 14 \) (solid lines) and \( n_{sc} = 28 \) (long dashed lines). All curves display the characteristic strain-stiffening behavior due to finite
extensibility of the intrinsically extended bottlebrush strands. As anticipated, the networks with smaller $n_x$ and larger $n_{sc}$ display more pronounced non-linearity due to greater extension of the network strands ($\beta \sim \sqrt{n_{sc} n_x^{-1}}$). The stress-strain curves in Fig. 3A are fitted using Eq. 1 with the two parameters introduced earlier: $G$ and $\beta$ (short dashed lines in Fig. 3A). Table 5.1 lists the regressed $G$ and $\beta$ values, as well as the apparent modulus ($G_0$) and elongation at break ($\lambda_{max,ex}$) measured at small and high strains, respectively. In Fig. 3B, the values of $G$ and $\beta$ are plotted as a function of $n_x^{-1}$ (an effective measure of crosslink density) and demonstrate excellent agreement with the scaling relationships provided in Eqs. 2 and 3. Such agreement highlights the consistency of both the bottlebrush architecture and the synthetic methods used to control it.

The strain-stiffening behavior apparent in Fig. 3A has direct implications for electroactuation, measured using the conventional diaphragm set-up pictured in Fig 2A and described in detail elsewhere (5). Figure 5.3C displays two characteristic examples of electroactuation for bottlebrush elastomers with and without EMI (see fig. S3 for more examples). In the first case, a PDMS bottlebrush elastomer with a short side chain ($n_{sc} = 14$) and long strand ($n_x = 200$) exhibits EMI, which is evidenced by a drastic snap-through at a constant nominal electric field $\Phi/d_0 = 7.6 \text{ V} \mu\text{m}^{-1}$. Note that the elastomer survives continued electroactuation from $\lambda_a^{EMI} \cong 1.6$ to $\lambda_a \cong 3.8$ and eventually undergoes dielectric breakdown at $\lambda_a^{BD} \cong 4.0$ and a true field of $33 \pm 5 \text{ V} \mu\text{m}^{-1}$ (fig. S4). Between $\lambda_a = 3.8$ and $\lambda_a^{BD} \cong 4.0$, electroactuation is stabilized by the finite extensibility of the network strands. The second example considered here (without EMI) corresponds to an elastomer with longer side chains ($n_{sc} = 28$) and exhibits steady voltage-controlled electroactuation over the entire extension.
range until dielectric breakdown occurs at $\lambda_{aBD} \cong 3.2$. In both instances, the experimental data points are consistent with theoretical predictions (solid lines in Fig. 3C and Eq. S4) given as

$$\frac{\Phi}{d_0} = (\epsilon \epsilon_0)^{-1/2} \sqrt{-\lambda^2 \sigma_{\text{true}}(\lambda) - \frac{PR}{4d_0} \frac{1}{\sqrt{\lambda^{-1} - 1}}}$$

(4)

where $\epsilon_0 = 8.85 \cdot 10^{-12} \text{F} \cdot \text{m}^{-1}$ is the dielectric permittivity of vacuum, $\epsilon = 2.94 \pm 0.02$ refers to the relative dielectric permittivity of the elastomer (fig. S5), $P = 5 \cdot 10^{-4} \text{atm}$ represents the blowing pressure to bias the actuation direction, and $R = 5 \text{mm}$ is the radius of the DE membrane. In addition to governing the strain-stiffening behavior, the parameter $\beta$ predicts the maximum extensibility of an ideal network as $\lambda_{max} \cong R_{max}/\sqrt{(R_{in}^2)} \cong \sqrt{\beta^{-1}}$. As evidenced in Fig. 3D and Table 5.1, the experimentally measured elongation at break ($\lambda_{max,ex}$) correlates reasonably well with the predicted $\lambda_{max}$. Note that, in our experiments (Fig. 3A), the $\lambda_{max,ex}$ values ranging from 1.9 to 3.5 mostly exceed the breakdown elongation $\lambda^{BD} = \sqrt{\lambda_{aBD}^{BD}} \cong 2$ (Fig. 3C).

In summary, we have developed a bottom-up synthetic strategy of single-component DEs that enable freestanding electroactuators to generate areal strains >300% and work densities ~20 kJ m$^{-3}$ at electromechanical efficiencies of ~93% under relatively mild field conditions (<10 Vµm$^{-1}$) that are on par with skeletal muscle. The molecular design approach to controlling (electro)mecanical developed here is independent of chemistry and permits access to an unprecedented range of actuation properties from materials with traditionally modest electroactuation performance (e.g., PDMS). The excellent baseline performance and myriad of chain-end functionalities afforded by the brush architecture open the use of
bottlebrush elastomers as a highly versatile platform for the creation of novel copolymers, composites, and physical networks for use in numerous soft-matter fields including dielectric actuators.\textsuperscript{11,28,29}
Figure 5.1: Electroactuation of pre-strained elastomers. (A) A dielectric elastomer sandwiched between two compliant electrodes undergoes uniaxial compression $\lambda = d/d_0$ and corresponding biaxial expansion upon application of an external electric field of potential $\Phi$. (B) Variation of the true stress as a function of the areal expansion $\lambda_a = \lambda^{-1}$ for three types of polymer networks: ① a conventional elastomer with coiled network strands that exhibit linear elasticity, wherein $\sigma(\lambda) \sim \lambda^2 - \lambda^{-1}$, ② an equibiaxially pre-strained conventional elastomer displays distinct strain-stiffening due to finite extensibility of the network strands, and ③ an elastomer with molecularly-strained network strands due to steric repulsion between densely grafted side chains, where $n_x$ – the degree of polymerization (DP) of the backbone in the bottlebrush strand, $n_{sc}$ – the DP of the side chains, and $n_g$ – the DP of the backbone spacer.
between neighboring side chains. (C) Nominal electric field (voltage normalized by \(d_0\)) as a function of areal expansion for the corresponding model elastomers described in (B). The broad red line indicates the region of electric breakdown, which depends on multiple experimental factors including thickness, anisotropic dielectric permittivity, and device construction.\(^{20}\) Dashed lines indicate continued electroactuation beyond the EMI.
Figure 5.2: Freestanding DE actuators. (A) Deflection of a circular diaphragm ($d_0 = 0.44$ mm) and (B) uniaxial extension and lateral dilation of a tube ($d_0 = 0.80$ mm and $D_0 = 11$ mm) are evident upon electroactuation with increasing voltage $\Phi$ (movies S1-S3). The numbers in (A) indicate field-induced areal expansion $\lambda_a = A/A_0 = d_0/d$ under isochoric conditions. The maximum strain achieved in the diaphragm and tube actuators was $\varepsilon_a = (\lambda_a - 1)100\% = 300 \pm 50\%$ and $25 \pm 5\%$, respectively. Both samples employ the same PDMS bottlebrush elastomer ($n_{sc} = 14, n_g = 1, n_x = 200$).
Figure 5.3: Electroactuation of bottlebrush elastomers. (A) True stress is presented as a function of uniaxial extension upon tensile deformation of bottlebrush elastomers with different crosslink densities ($\sim n_x^{-1}$) and side-chain DPs ($n_{sc}$). The color-matched solid and long dashed lines correspond to the sample series with $n_{sc} = 14$ and 28, (corresponding $n_x$ values are indicated in plain and bold, respectively. (B) The shear modulus ($G$) and elongation ratio ($\beta$) extracted from fitting the stress-strain curves in (A) with Eq. 1 (short dashed lines) are plotted as a function of $n_x^{-1}$. In accord with theoretical predictions, both properties increase linearly with increasing crosslink density. From the corresponding slopes and the known values of $n_{sc} = 14$, $n_g = 1$, and $\rho = 7.7$ nm$^{-3}$ for PDMS, we obtain the numerical prefactors $C_1 = 0.3$ and $C_2 = 3.1$ in Eqs. 2 and 3. (C) Electroactuation of two bottlebrush elastomers with the
same network strand DP ($n_x = 200$) and two different side-chain DPs: 14 and 28. The experimental data points display favorable agreement with theoretical predictions (solid lines). The 10% offset in actuation is due to the biasing pressure $P = 5 \cdot 10^{-4}$ atm (Eq. 4). The experimental elongation at break ($\lambda_{max,ex}$) of the bottlebrush elastomers with $n_{sc} = 14$ is linearly dependent on the initial strand elongation $\sqrt{\beta^{-1}}$ (Eq. 3).
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<th>n_{x}^{b}</th>
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<th>G (kPa)^{d}</th>
<th>\beta^{e}</th>
<th>G_0 (kPa)^{f}</th>
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a) Degree of polymerization (DP) of the sidechain (Fig. 1B). b) Targeted DP of the backbone between crosslinks calculated from the mole fraction of the difunctional crosslinker as \( n_x = 1/(2\phi_x) \). Although the actual \( n_x \) values may be larger due to incomplete conversion of the crosslinker moieties, precise control of the crosslink density as linearly proportional to \( n_x^{-1} \) is accomplished (Fig. 3B). c) Mole fraction of crosslinker used in the synthesis. d) Structural shear modulus and e) elongation of network strands in as-prepared bottlebrush elastomers determined by fitting the stress-strain curves in Fig. 3A with Eq. 1. f) Apparent shear modulus measured as the slope \( G_0 = d\sigma/d\lambda \) at small deformations \( (\lambda \rightarrow 1) \). g) Maximum uniaxial extension calculated as \( \sqrt{\beta^{-1}} \). h) Experimentally measured elongation at break.
References


**Acknowledgments:**

The authors gratefully acknowledge funding from the National Science Foundation (DMR 1122483, DMR 1407645, DMR 1436201, and DMR 1409710) and from Becton Dickinson Technologies. We also thank Dr. Edward Samulski for illuminating discussions and reviewing the manuscript.
Supplementary Materials

Synthesis and characterization

Materials: Monomethacryloxypropyl-terminated poly(dimethylsiloxane) (MCR-M11, with an average molar mass of 1000 g/mol), monoaminopropyl-terminated polydimethylsiloxane (MCR-A12 with an average molecular mass of 2000 g/mol) and α,ω-methacryloxypropyl-terminated poly(dimethylsiloxane) (DMS-R18 and DMS-R22 with two different average molar masses of 5000 and 10000 g/mol, respectively) were purchased from Gelest. All macromonomers were purified by passing them through a basic alumina column to remove the inhibitor. Methacryloyl chloride (purity >97%), phenylbis(2,4,6-trimethyl-benzoyl)phosphine oxide, triethylamine (TEA), copper chloride, tris[2-(dimethylamino)ethyl]amine (Me₆TREN), ethyl-2-bromo-2-methylpropionate, dimethyl formaldehyde (DMF), tetrahydrofuran (THF), p-xylene (PX) were all purchased from Aldrich and used as-received. All other reagents and solvents were purchased from Aldrich and used without further purification.

Monomethacryloxypropyl-terminated poly(dimethylsiloxane) (M12, with an average molar mass 2000 g/mol): Monoaminopropyl terminated poly(dimethylsiloxane) (MCR-A12, 40 g, 20 mmol), anhydrous methylene dichloride (DCM, 100 mL), and triethylamine (3.5 mL) were added to a 250 ml round-bottom flask under nitrogen. The reaction mixture was cooled in an ice bath, followed by injection of methacryloyl chloride (2.3 g diluted in 3 mL DCM) over 30 min. Upon addition, the reaction mixture was allowed to reach ambient temperature and stirred overnight. The solid portion of the mixture was separated by filtration, and the filtrate was washed 3x with dilute sodium hydroxide solution (0.2 M, 150 mL), followed by
washing with deionized water (3 x 150 mL). The mixture was dried by adding magnesium sulfate, passed through a basic alumina column to remove remaining inhibitor from the methacryloyl chloride, and stored in a freezer (-20 °C).

**Poly(dimethylsiloxane) bottlebrushes.** A 25 mL Schlenk flask equipped with a stir bar was charged with ethyl-2-bromo-2-methylpropionate (2.4 mg, 12.5 µmol), monomethacryloxypropyl-terminated poly(dimethylsiloxane) (MCR-M11; 15.0 g, 15.0 mmol), Me₆TREN (2.9 mg, 3.3 µL), and p-xylene (12.0 mL). The solution was bubbled using dry nitrogen for 1 h. Then, CuICl (1.2 mg, 0.012 mmol) was quickly added to the reaction mixture under nitrogen. The flask was sealed, back-filled with nitrogen, purged for 5 min, and then immersed in an oil bath thermostated at 45 °C. The polymerization was stopped after 10 h, and the monomer conversion was determined by ¹H NMR (85%), resulting in a bottlebrush PDMS polymer with a backbone DP of $n_{bb} \approx 1200$. The polymer was purified by thrice precipitation from dimethyl formaldehyde and dried under vacuum at ambient temperature until a stable mass was obtained.

To display the unentangled nature of PDMS bottlebrush polymers, a rheological master curve was produced for a sample with $n_{bb} = 1200$ (nearly 10x the entanglement length of linear PDMS) and $n_{sc} = 14$. The frequency ($\omega$) dependence of the dynamic moduli (storage modulus $G'$ and loss modulus $G''$) was measured from 0.1 to 100 rad/s over temperatures ranging from 303 to 153 K and strains ranging from 0.1 to 5% using an ARES-G2 rheometer (TA Instruments). Multiple measurements at different strains at a single temperature were performed to ensure a linear response. The time-temperature superposition principle was used
to construct master curves of modulus versus frequency with a reference temperature of 298 K using the Williams-Landel-Ferry (WLF) equation. Fig. S1A displays a master curve of a PDMS bottlebrush exhibiting distinctly unentangled Rouse-like behavior prior to terminal relaxation (range 1). The weak plateau observed at higher frequency (range 2) is due to relaxation of linear chain segments as they undergo dynamic coupling with the backbone.

The samples examined by atomic force microscopy (AFM) were prepared by spin-casting a 0.05 mg/ml polymer solution in chloroform at a rate of 2000 rpm for 1 min onto freshly-cleaved mica. Images of individual molecules were acquired in PeakForce QNM mode using a multimode AFM (Brüker) with a NanoScope V controller. Silicon probes were used with a resonance frequency of 50-90 Hz and a spring constant of ~0.4 N/m. Fig. S1B displays a height image of PDMS bottlebrush macromolecules with $n_{bb} = 1200$ and $n_{sc} = 14$, which shows well-defined worm-like macromolecules, highlighting the segregation of bottlebrush macromolecules because of side-chain steric repulsion. The inset demonstrates the flexible character of an individual bottlebrush macromolecule.

**Preparation of elastomer films and tubes.** All elastomers were prepared by one-step polymerization of monomethacryloxypropyl-terminated PDMS (MCR-M11, 1000 g/mol; MCR-M12, 2000 g/mol) with different molar ratios of crosslinker (DMS-R18 and DMS-R22 for making elastomers with M11 and M12, respectively) (Fig. S2). The initial reaction mixture contained 57 wt% of the monomers (M11 or M12), varying ratios of R18 or R22 as crosslinker, 32 mg of phenylbis(2,4,6-trimethyl-benzoyl)phosphine oxide as the photo-initiator, and 9 g of $p$-xylene as a solvent. The mixtures of monomer (M11 or M12), cross-linker and photo-
initiator in $p$-xylene were degassed by nitrogen bubbling for 30 min. For preparation of an elastomer film, the mixtures were injected between two glass plates with different spacers (in mm): 0.25, 0.5, 1.0 and 3.0. The resulting elastomer films were then allowed to polymerize at ambient temperature under nitrogen using a UV cross-linking chamber equipped with a 365 nm UV lamp for 12 h (0.1 mW/cm$^2$, 10 cm distance). Elastomer tubes were prepared by injecting the above mixtures between two concentric cylindrical molds with inner and outer diameters of 9.5 mm and 12.5 mm, respectively, and repeating the above curing procedure. Films and tubes were subsequently swollen in chloroform in a glass Petri dish. After 8 h, the chloroform was replaced with fresh chloroform to remove unreacted monomer. This washing cycle was repeated several times, after which the samples were deswollen with ethanol and dried in an oven at 50°C. The conversion of monomer to elastomer (gel fraction) was measured between 87 to 95 wt% from

$$\text{Monomer conversion (gel fraction)} = \frac{\text{Mass of sample before washing}}{\text{Mass of sample after washing}} \times 100\% \quad (S1)$$

**Deflection of a pressurized diaphragm**

We start by considering a capacitor with compliant electrodes acting as a spherical cap of radius $R$ to a chamber maintained at a pressure $P$ (Figure 5.6). The space between the plates of the capacitor is filled with a bottlebrush elastomer with dielectric constant $\varepsilon$. Initially, the two electrodes are separated by a distance of $d_0$ and have areas $S_{sc0}$. By applying a voltage $\Phi$ across the capacitor plates, we force the elastic material to shrink under isochoric conditions, increasing the height ($h$) and surface area $S_{sc}(h) = \pi(h^2 + R^2)$ of the spherical cap and decreasing the total free energy of the system. At constant volume ($V = \pi d(h^2 + R^2)$ =
\( \pi d_0 R^2 \) of the elastomer, the gap between the plates decreases by a factor \( \lambda \) as \( d = d_0 \lambda \), and the height of the cap increases as \( h(\lambda) = R \sqrt{\lambda^{-1} - 1} \). The volume under the spherical cap capacitor also increases as a function of \( \lambda \), where \( V_{sc}(\lambda) = \pi h(h^2/6 + R^2/2) \). At \( d \ll R \), we can approximate the system as a plate capacitor. In this case, the capacitance \( C \) decreases by a factor \( \lambda^2 \) as \( C = C_0/\lambda^2 \), with respect to that of the undeformed capacitor \( C_0 = \varepsilon_0 A_0 / d_0 = \varepsilon_0 V/d_0^2 \). The total free energy change upon capacitor deformation (\( \Delta F \)) includes the change in the electrostatic energy stored in a capacitor, the elastic energy of the deformed bottlebrush network, and the work done on the system by increasing the volume under the spherical cap as

\[
\Delta F(\Phi, P, \lambda) \approx -\frac{C_0 \Phi^2}{2\lambda^2} + GV \left[ \frac{I_1(\lambda)}{6} + \beta^{-1} \left( 1 - \frac{\beta I_1(\lambda)}{3} \right)^{-1} \right] - PV_{sc}(\lambda) \quad (S2)
\]

where \( G \) is the shear modulus of the elastomer, \( I_1(\lambda) = \lambda^2 + 2/\lambda \) is the first deformation invariant for uniaxial deformation, and parameter \( \beta = R_{max} b_k / R_{max}^2 \approx b_k / R_{max} \) is the network strand elongation ratio. Minimization of the free energy (Eq. S2) with respect to \( \lambda \) yields the equation relating applied voltage \( \Phi \) to bottlebrush network deformation, viz.,

\[
\frac{C_0 \Phi^2}{\lambda^3} + \frac{GV}{3} (\lambda - \lambda^{-2}) \left[ 1 + 2 \left( 1 - \frac{\beta I_1(\lambda)}{3} \right)^{-2} \right] + \frac{PR^3 \pi}{4} \frac{1}{\lambda^3 \sqrt{\lambda^{-1} - 1}} = 0 \quad (S3)
\]

Equation S3 is more convenient to solve for the field potential \( \Phi \) as a function of \( \lambda \) as

\[
\Phi = \frac{d_0}{\sqrt{\varepsilon \varepsilon_0}} \sqrt{-\lambda^2 \sigma_{true}(\lambda) - \frac{PR}{4d_0 \sqrt{\lambda^{-1} - 1}}} \quad (S4)
\]

where \( \sigma_{true}(\lambda) \) is the true stress in the material and increases with compression \( \lambda \) according to

\[
\sigma_{true}(\lambda) = \frac{G}{3} (\lambda^2 - \lambda^{-1}) \left[ 1 + 2 \left( 1 - \frac{\beta I_1(\lambda)}{3} \right)^{-2} \right] \quad (S5)
\]
Note that the solution of eq. S4 only exists for the compression region \((\lambda < 1 \text{ and } \sigma_{\text{true}}(\lambda) < 0)\). When no bias pressure is applied, eq. S4 reduces to conventional models. The capacitor discharges when the field inside the capacitor becomes larger that the critical electric field \(E^*\). Taking into account the relation between electric field and voltage \(\Phi\), we obtain

\[
\Phi^*(\lambda) = \lambda d_0 E^*
\]  

(S6)

It is important to point out that the breakdown field is not a material characteristic, since it depends on several experimental parameters including film thickness, inherent heterogeneities, and orientation of polymer chains. For example, the experimental data and theoretical predictions in Fig. S3 indicate that the dielectric breakdown (BD) increases with increasing crosslink density \((\sim n^{-1})\), and Fig. S4 reveals that the BD likewise increases with decreasing film thickness. Measured values of the dielectric constant at ambient temperature are also observed in Fig. S5 to change with frequency for PDMS bottlebrush elastomers, whereas they do not for a linear PDMS elastomer.
Figure 5.4 (A) Rheological master curve of a unentangled PDMS bottlebrush melt (uncrosslinked) prepared by atom-transfer radical polymerization (ATRP) of monomethacryloxypropyl-terminated poly(dimethylsiloxane), as explained in the text. Materials display completely unentangled Rouse-like behavior (range 1) prior to terminal relaxation. The indistinct plateau (range 2) is due to relaxation of side-chain segments. (B) AFM height images of a monolayer of a bottlebrush macromolecules ($n_{bb} = 1200$ and $n_{sc} = 14$) deposited on a mica substrate. The images display individual worm-like molecules, which are well-segregated because of the side chains.
Figure 5.5 Synthesis of bottlebrush macromolecules and bottlebrush elastomers by photo-initiated radical polymerization of monofunctional macromonomers in the presence of a difunctional crosslinker DMS-R18 and DMS-R22 having DP of q=62 and 130, respectively.
**Figure 5.6.** Schematic of diaphragm actuator used in our experimental setup.

**Figure 5.7** Electroactuation of PDMS bottlebrush elastomers. Theoretical curves (solid lines) and experimental data (square symbols) correspond to electric field vs. areal expansion during voltage-controlled uniaxial compression at nearly zero bias pressure ($P = 10 \text{ Pa} \ll 1 \text{ atm}$). Calculations and measurements were performed for two sets of PDMS bottlebrush elastomers possessing different side-chain DPs – (**A**) $n_{sc} = 14$ and (**B**) $n_{sc} = 28$ – and varying values of $n_x$ as indicated. The theoretical lines were calculated using eq. S4 for the case of $P = 10 \text{ Pa}$. 

![Schematic of diaphragm actuator](image-url)
Figure 5.8 The dielectric strength (breakdown field) of a PDMS bottlebrush elastomer ($n_{sc} = 14$, $n_x = 50$) was measured for as-cast films of different thicknesses. A linear PDMS elastomer was also measured as a reference sample. The fitting equation in the upper-right corner corresponds to the bottlebrush sample. For a typical $d_0 = 0.44 \text{ mm}$ and $\lambda_{a BD} \cong 4.0$, the breakdown occurs at an electric field of $33 \pm 5 \text{ V\mu m}^{-1}$ corresponding to a film thickness of $d = d_0/\lambda_{a BD} \cong 110 \text{ \mu m}$.
Figure 5.9 The dielectric constant of a linear PDMS elastomer and four PDMS bottlebrush elastomers ($n_{sc} = 14$) with different crosslink densities characterized by $n_x^{-1}$ (as labeled) was measured at varying frequencies from 20 Hz to 1 MHz. The circles correspond to experimental data points and solid lines are drawn as a guide for the eye. For the upper three samples ($n_x = 67, 100$ and 200), only the guiding lines are presented for clarity.
Electroactive Shape Memory: A Thermoplastic Elastomer Gel as a Bimorphic Dielectric Elastomer

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Dielectric elastomer actuators (DEAs) are a class of soft actuators that have found great promise in dynamic and responsive operation scenarios. For example, micropumps, vibration control, prosthetics and multitudinous other applications have all employed traditional DEAs to great effect. The properties of DEAs are suitable for dynamic applications considering rapid response times and broad mechanical bandwidth (10s of kHz to as low as µHz and static operation), with the added benefits of high transduction efficiency and quiet operation. Still, there are particular applications in quasi-static systems for which dielectric elastomers are not suitable or at least offer substantial engineering challenges.

The principal issues of low frequency and static DE operation are energy loss due to leakage current and constant high voltage polarization. Current leakage could have large implications in applications such as spaceflight and satellite technology where energy expenditure comes at a premium, and high voltage polarization constitutes an issue for human interactions with soft robots due to safety concerns. Dynamically responsive DEAs require an electrical energy input to maintain strain-fixity, but a low frequency operation actuator would ideally have zero-energy fixity with only periodic energy inputs for changes to actuation state. In this work, we hope to present a viable option for a static DEA that uses a thermally
triggered shape memory elastomer to impart zero-energy fixity. We employ a thermoplastic elastomer gel with temperature responsive shape memory capabilities\textsuperscript{13} that demonstrates a massive change in mechanical stiffness as a “bimorphic” dielectric elastomer that can exist at multiple strain states with zero electrical energy input.

The thermoplastic elastomer gel (TPEG) system has design parameters based on established, successful dynamic dielectric elastomers.\textsuperscript{14–16} The gel is composed of a triblock copolymer, poly(styrene-\textit{b}-ethylene-\textit{co}-butylene-\textit{b}-styrene) (SEBS, Kraton G1651), and a midblock selective solvent, icosane (C\textsubscript{20}H\textsubscript{42}, T\textsubscript{melt}= 36-37°C) an aliphatic, low polydispersity paraffin wax. Mechanical and morphological properties of similar TPEG systems have been described in detail in the literature.\textsuperscript{13,17} The mechanism for shape memory in this material depends on the formation of two networks: (1) a semi-permanent shape is formed by the microphase separation of the block copolymer, and (2) a secondary network is formed when icosane crystals form into each other to make a percolated network of interlocking crystallites.

Styrenic endblocks form physical crosslinks below the glass transition temperature (~95°C), deemed a “semi-permanent” network as physical crosslinks can be rearranged when above the glass transition temperature. The insets in Figure 6.1 shows a nanoscale schematic of a TPEG network. Due to the architecture of SEBS used herein (~30% styrene and 70% ethylene-\textit{co}-butylene content), a nanoscale morphology of styrenic spheres in a continuous matrix of ethylene butylene and aliphatic icosane solvent phase is presumed to be adopted across all possible gel fractions of the elastomer,\textsuperscript{18–20} though some changes in nanostructure were measured during the crystallization process.
In addition to introducing this material as a novel DEA, we demonstrate a controlled heating process and accompanying model to predict the film temperature. The heating mechanism involves no additional electrical components and passive cooling by applying a high frequency AC signal across the DEA. A combination of dielectric losses and resistive losses manifest as heat. Figure 6.1 describes the bimorphic DEA process with relevant thermal and electrical states.

**Fabrication of Bimorphic DEA**

Our bimorphic DEA consists of a shape memory thermoplastic elastomer as the dielectric and a carbon nanofiber composite as a compliant electrode. In a precursor to this work, details of morphological and mechanical properties as well as casting procedures of the shape memory films have been described by Mineart et al.\textsuperscript{13} The thermoplastic elastomer used in this work is poly\{styrene-\textit{b}-ethylene-\textit{co}-butylene-\textit{b}-styrene\} manufactured by Kraton Polymers (Grade 1651). It is solution cast from toluene with two additional components 1) a linear, saturated paraffin wax, icosane (C\textsubscript{20}H\textsubscript{42}, Fisher Scientific), and 2) a glassy hydrocarbon tackifier (Exxon 5380). The composition of a shape memory elastomer is described as S/C/T:xx/yy/zz where S, C and T indicate polymer, paraffin and tackifier, respectively, and xx, yy, and zz indicate the mass fractions (%) of each of the corresponding components. Electrodes are fabricated by adding carbon nanofiber to the shape memory elastomer (Sigma Aldrich) during the casting process. The electrodes are cast from tetrahydrofuran onto a heated surface (50°C) to rapidly drive off solvent. The electrodes are applied directly to the surface of the dielectric and thermally welded together. Further details are given in supplementary
information Figure S6.1. A silicone grease is also used for electroactuation measurements so as not to impede the actuation strain.

**Temperature Control of a DEA**

Generally, dielectric loss is considered a design challenge for dynamic DEAs. Dielectric loss has an energy cost per cycle, and it can reduce device efficiency. The primary mechanism for dielectric energy loss generates heat as waste energy. The dielectric power loss per unit volume for a capacitor in an AC field \( P_D \) is a function of the frequency \( \omega \), voltage \( \Phi \), and dielectric loss, \( \varepsilon'' \) such that

\[
P_D = \omega \varepsilon_0 \varepsilon'' \left( \frac{\Phi}{d} \right)^2 V
\]

Eqn. 6.1

where \( \varepsilon_0 \) is the permittivity of free space, \( d \) is the thickness of a dielectric film and \( V \) is the volume of the capacitor. At high frequency and field strength, the power generation due to dielectric loss can be significant. Taking advantage of this, we can use the alternation of AC and DC biasing at high voltage to switch between a heating state and an actuating state. While this is intended to be the primary heating mechanism, there are other potential mechanisms responsible for heat generation, specifically joule heating and mechanical losses. We have neglected mechanical losses as they are only of consequence at frequencies below mechanical resonance.

In a high frequency system, current flow across the capacitor is substantial; for the system described here, current fluxes are on the order of \( 10^3 \) A mm\(^{-2} \) (currents of \( \sim 10^{-1} \) mA). For good conductors, *e.g.* copper electrodes (\( \sigma \sim 6 \times 10^7 \) S/m), the magnitude of resistive heating is not a major contributor to heat generation. For many flexible electrode materials
used in DEAs, i.e. carbon based greases, graphite, carbon fiber and nanotubes, metallic particles and pastes, conductivity is much lower ($\sigma \sim 10^{-5} - 10^{-3}$ S/cm), and there is considerable contribution due to resistive heating. Power generated from joule heating ($P_I$) is

$$P_I = I_{RMS}^2 R = \Phi_{RMS}^2 / R$$

Eqn. 6.2

where $I_{RMS}$ and $\Phi_{RMS}$ are the root mean squared current and voltage, respectively. The sum of these two heat generation terms are responsible (within our model) for all forms of heat generation.

$$\dot{H}_{gen}(\Phi, \omega, d) = P_D + P_I = (V)\omega \varepsilon_0 \varepsilon'' \left(\frac{\Phi}{d}\right)^2 + \Phi_{RMS}^2 \omega$$

Eqn. 6.3

where $r$ is resistivity of the electrode material, $I$ is current and $L$ and $w$ are electrode dimensions length and width, respectively. The current is calculated from the capacitance and the frequency as current is equal to

$$I = \left(\frac{\varepsilon_0 \varepsilon'(w+l)}{d}\right) \ast \left(\frac{d\Phi}{dt}\right)$$

Eqn. 6.4

where the change voltage rate change of a triangular wave is taken as $\left(\frac{d\Phi}{dt}\right) = \Phi_{RMS} \omega$. The only electronics necessary are those already present in DEAs, an arbitrary waveform generator, a voltage amplifier and DEA components.

While modelling power generation is relatively straightforward, predicting the steady-state temperature of a DEA film at a particular set of conditions (particularly voltage, frequency and geometric considerations) requires understanding of the heat loss mechanisms. The general term for heat loss generation is defined as

$$\dot{H}_{loss}(T) = h(w \ast L)(T_s - T_a)$$

Eqn. 6.5.
where \( T_s \) and \( T_a \) are the surface and ambient temperatures, respectively. For the purposes of this model, we have considered a flat plate geometry and free convection heat loss. A heat transfer coefficient can be calculated from the Nusselt number and a correlation for flat plate geometry.\(^{24}\)

\[
Nu = \frac{hL}{k} = (0.54) \left( \frac{g \beta \rho}{\nu \alpha} (T_s - T_a) L^3 \right)^{1/4}
\]

Eqn. 6.6.

The values of the constants used for analysis are given in supplementary information (Table S6.1).

For sensible heat changes of a DEA film, we can calculate the surface temperature using the differential equation

\[
\rho C_p \left( \frac{dT}{dt} \right) = P_D + P_I - \dot{H}_{loss}
\]

Eqn. 6.7

where \( \rho \) and \( C_p \) are the density and specific heat capacity of the active area of the dielectric film. Equation 6 is a separable differential equation that takes the form

\[
dt = \left[ G - K(\Delta T)^{5/4} \right] d\Delta T
\]

Eqn. 6.8

with values \( G \) and \( K \) being groupings of constants (again see Table S6.1) and \( \Delta T = T_s - T_a \). We have solved this differential equation numerically, though there is an analytical solution.

For first order phase transitions (melting of paraffin), since there is no temperature change, a melting time can instead be calculated as

\[
t_{melt} = \frac{\rho V \Delta H_{fus}}{P_D + P_I - \dot{H}_{loss}}
\]

Eqn. 6.9.

The model is applied as piecewise functions with discontinuities at the phase transition temperature throughout melting. It should be noted that conductivity has been treated as a constant rather than a function of temperature, and conductive heat transfer effects from the
electrode inward were considered to be negligible due to the small film thickness and the uniform heating of the dielectric mechanism.

The result of this model is a rather complex system where current (and therefore the joule heating contribution) is dependent on the capacitance of the system as well as the temperature. In the case of high conductivity electrodes, the contributions of $P_I$ are negligible. These systems where $P_I$ dominates as the mechanism for power generation, the coupling is less pronounced, and straightforward predictions can be used to estimate temperature from only frequency and voltage (Figure S6.2). To validate the model for sensible heat changes, a model dielectric material was used (polyimide, Kapton HN film). Figure 6.2A shows a series of infrared images of a capacitor formed from circular copper electrodes and the model dielectric.

Using carbon nanofiber electrodes, $P_D$ contributes substantially to the overall power generation. Figure 6.2B demonstrates how stepwise voltage changes affect steady-state temperature. Voltage is periodically incremented at 30 second time steps to allow temperature equilibration. Each voltage step of 500 V corresponds to an electric field strength of 4.2 V/mm. Regardless of the mechanism of heat generation, the system initially heats rapidly before settling around a steady-state temperature. In addition to voltage control, it is possible to use varying frequency to control steady state temperature. Figure 6.2C shows the effect of frequency changes on a bimorph DEA. At temperatures higher than the melting point of a bimorph DEA, runaway temperature rises that lead to catastrophic failure are commonly observed. This type of behavior is not observed in the model polyimide film.
Electroactuation

Bimorphic DEA films were used to study the electroactive behavior. These films were modeled in composition off of previous work with thermoplastic elastomer gel based DEAs. Due to lower miscibility of paraffin with SEBS copolymers, polymer fractions are limited to 20 weight percent or greater. Electroactuation tests were done by uniformly heating a prestrained elastomer DEA then applying an incremental voltage. The bimorph DEA of composition S/C/T:30/50/20 is equibiaxially prestrained (200% x 200%) and heated to 50°C in an oven enclosure. A stepwise increase in voltage yields an areal strain response measured by a digital camera. Because the mechanics so closely match those of TPEGs, the electromechanical response of S/C/T:30/50/20 is expected to be similar to the response of a 30% SEBS gel with mineral oil solvent (data for SEBS/MO:30/70 wt% reproduced from Krishnan et al.).

Figure 6.3A compares the actuation response of these two elastomers under the same prestrain conditions (200% x 200%). The response between elastomers is similar with areal actuation strains of 36% and 39% achieved at 50 kV/mm and 63 kV/mm for SEBS/MO:30/70 and S/C/T:30/50/20 respectively. Differences are attributed to the effects of tackifier on mechanical response. Although both TPEGs are capable of higher actuation strains (>100%) due to electromechanical instability, the snap-through nature of the actuation makes small changes in voltage likely to lead to breakdown. Additionally, elevated temperature decreases breakdown strength and long crystallization time may be responsible for creep. The crystallization time of the bimorphic S/C/T:30/50/20 in Figure 6.3A was 30 minutes at room temperature to ensure complete formation of a paraffin crystalline network. Figure S6.3 shows
rheological data to demonstrate the time scale of crystallization, ensuring that crystallization is effectively complete at 30 minutes.

Figure S6.4 shows the tensile strain fixity of S/C/T:30/50/20 cooled in air at room temperature (23°C). Strain fixity, $f_t$, as a percentage is defined as

$$f_t = 100 \times \frac{\varepsilon_f}{\varepsilon_s} \quad \text{Eqn. 6.10.}$$

where $\varepsilon_s$ and $\varepsilon_f$ are the maximum applied strain and the fixed strain after removal of external stress, respectively. The strain fixity as $t \to \infty$, $f_\infty$, is calculated to be 95%. This corresponds well with electroactuation results of S/C/T:30/50/20 that show about 96% strain fixity relative to the initial actuation strain achieved. During the crystallization process, we believe that the shrinkage of the film due to densification is a major contributor to imperfect strain fixity. Once crystallized, the removal of electric polarization seems to have near perfect strain fixity.

**Conclusions and Future Outlook**

Because of the large contribution to heat generation due to joule heating, the topology and quality of electrodes is of extreme importance. More thorough investigation and a more robust deposition method is required for reliable heating and current flow. Electrodes in the current study had poor control on film thickness of electrodes and showed non-uniform heating in some experiments. Additionally, more in depth exploration of the effects of degree of prestrain on actuation behavior are required. The mechanical integrity of the shape memory polymer was lower than expected for a thermoplastic elastomer, likely due to some degree of macroscopic phase separation as suggested in previous work\textsuperscript{13,17} and macroscopic observations of liquid films forming on polymer gels following heating above the melting point of the paraffin.
As to the choice of material selection of the dielectric, there would be some substantial benefits to employing a shape memory polymer with higher dielectric constant and dielectric loss. Some alternatives are proposed in the future work section (Chapter 8). Validation experiments presented here using polyimide were quite successful as the material properties are well suited for capacitive heating in the kHz frequency range. Operating at higher frequency becomes problematic for low conductivity electrodes due to the high voltage required for substantial current flow that will exceed the breakdown strength of the dielectric. We believe that the use of a thermoplastic elastomer with more favorable electrical properties would perform effectively with the system designed in this work.
Figure 6.1. The proposed process of bimorphic shape memory using a dielectric elastomer film. Blue indicates temperatures below the hydrocarbon melting point and red indicates temperatures above the melting point. Black arrows designation a change in electrical charge state (i.e. DC biasing). In state (A), a dielectric elastomer film with compliant electrodes exists in a state of no applied voltage ($V = 0$) and a temperature below the melting point ($T < T_m$). The inset shows a block copolymer network wherein the elastic chains are immobilized by a network of paraffin crystallites. In state (B), a high frequency electric field is applied across the DEA ($\omega \sim 10$ kHz, above the resonant mechanical frequency). Energy is dissipated by mechanical loss, dielectric loss and joule heating to heat the DEA to a temperature $T > T_m$. The inset of (B) shows the thermoplastic elastomer network in a midblock selective liquid solvent that exhibits the behavior of a thermoplastic elastomer gel. In state (C), the high frequency signal is rectified to a high voltage DC signal and the DEA actuates by a reduction in thickness across the capacitor and an increase in area of the electrode. In state (D), the film is passively cooled due to ambient heat loss while a DC bias is maintained ($V > 0$). At a high degree of crystallinity, the electrical bias is removed (A’). The shape memory elastomers mechanics are dominated by the crystalline midblock solvent as two networks reach equilibrium, 1) the
thermoplastic elastomer network in tension, and 2) the paraffin crystalline network in compression. Because of the drastic difference in stiffness between the two networks, high strain fixity is achieved and the bimorphic dielectric elastomer can exist at multiple strain states under a zero voltage condition. Heating the elastomer in the (A’) state will return the elastomer to the soft state at point (B).
Figure 6.2. A) Kapton HN film used for validation of the dielectric heating thermal model. A circular copper foil electrode is used so that the joule heating contribution is negligible. The AC field applied is 10 kHz at 4 kV_{p-p}. B) A 13 kHz signal is applied at various voltages. The electrodes are carbon nanofiber with dimensions 3 x 1 cm² with a 2 x 1 cm² active capacitive area across a 120 micron thick film. The red line (—) indicates the voltage which was incremented in step changes, the blue line (—) indicates the model predictions for T(t), and the blue circles (○) indicate data from infrared camera measurements. C) The effects of frequency variation on temperature of a bimorphic DEA. Application voltage is 2.8 kV_{p-p} corresponding to a field strength of 9 kV/mm. D) Infrared time lapse images of copper electrodes undergoing dielectric heating (data corresponding to Figure 6.2A.)
Figure 6.3. A) Electroactuation of a bimorphic dielectric elastomer. Bimorphic dielectric elastomer S/C/T:30/50/20 is shown in red (1<sup>st</sup> cycle - ○, 2<sup>nd</sup> cycle - ●), while dielectric elastomer SEBS/MO:30/70 is shown in blue (●). Strain fixity is nearly perfect, though there is measured area change due to densification of the film during crystallization.
Supplementary Information

Figure S6.1. Carbon nanofiber composite elastomer synthesis is depicted and conductivity measurements are made.
Figure S6.2. Simple predictions for melt time of a 1mm thickness bimorph DEA based on the dielectric heating contribution without heat losses.
Figure S6.3. Shear rheological measurements of S/C/T films to study the effects of crystallization on mechanics. A) Changes in shear modulus of S/C/T films over time are given as a ratio of the initial modulus of the gel ($G'_0 = G'$ at 50°C where $T > T_{melt}$). Different conditions are shown by each data set: red circles (●) are S/C/T:30/50/20 crystallized at 35°C, light blue circles (●) are S/C/T:30/50/20 crystallized at a cooling rate of 5°C/min, dark blue circles (●) are S/C/T:30/50/20 crystallized at 2°C/min, and black triangles (▲) are S/C/T:20/80/00 crystallized at 2°C/min. The plateau modulus is much higher with high concentrations of paraffin due to the highly percolated network of paraffin crystals. The plateau modulus of S/C/T:20/80/00 is approximately 4*10^7 and the plateau modulus of S/C/T:30/50/20 is ~1*10^6. B) Temperature sweep of S/C/T:20/80/00
Figure S6.4. Strain fixity of S/C/T:30/50/20 in tensile extension. Set strain is 300%. Fit with a first order exponential of the form $f_t = f_\infty (1 - e^{-k(t-t_{lag})})$, where $k$ is a crystallization rate constant, $t_{lag}$ is a constant associated with crystal nucleation, and $f_t$ is the strain fixity as a function of time. The strain fixity as $t \to \infty$, $f_\infty$, is calculated to be 95%. This corresponds well with electroactuation results of S/C/T:30/50/20.
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Form Stable Phase Change Materials from Fatty Acids and Thermoplastic Copolyesters

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Phase change materials (PCMs) have been of considerable interest to the scientific community for thermal energy storage applications over many decades. These materials have found application in climate control,¹–³ insulation⁴ and thermal energy storage,⁵,⁶ but the adoption of PCMs in a broad commercial sense has been rather slow despite the long history. Primarily, this is due to the challenge of encapsulation. By nature, solid-liquid, liquid-gas and solid-gas transitions involve changes in volume. Condensed phase to gas phase transitions have massive volume changes and make engineering design of encapsulates challenging and cost prohibitive despite sizable latent heats. Solid-liquid and solid-solid transitions are much more manageable in terms of volume changes. Solid-solid transitions often have low enthalpy, and the flow of liquids still requires a form of encapsulation. Encapsulates have been developed by polymerizing shells around a solid-liquid phase change material.⁷–⁹ These encapsulates are necessary for the long term performance of PCMs.

In this study, we are investigating the use of a more elegant solution to solvent containment: polymer gel systems containing a PCM as the solvent. These non-encapsulated materials are known in the PCM literature as “form-stable” PCMs because the network forming portion of the PCM composite exhibits solid-like mechanical properties in both the solid and liquid states of the PCM. For consistency, we will abide by the form-stable nomenclature,
though form-stable can include systems other than polymer gels.\textsuperscript{10} Form-stable PCMs generally consist of two components: 1) a network forming polymer or solid binder that can be chemically (irreversibly) or physically (reversibly) crosslinked, and 2) a solvent that undergoes a first order phase change (melting/crystallization) at a desired temperature.

A wide range of materials are available for both network formers (e.g. block copolymers and other elastomers) as well as PCMs. Generally, PCMs are split into two categories, organic and inorganic wherein the organics contain crystalline small molecules such as paraffins and fatty acids, and the inorganics of broad interest are various salt hydrates. Notably, organics tend to have lower melting points than inorganic PCMs, and also have higher solubility and compatibility with polymer systems. Liquid-liquid solubility between polymer networks and organic PCMs allows for the formation of a single phase in the liquid state without encapsulation. This process has advantages over encapsulated PCMs in regard to fabrication simplicity and processability as network former and PCM can be mixed in a manner congruous with existing polymer processing techniques (e.g. melt mixing or in-situ polymerization).

Our particular system uses thermoplastic copolyesters as network formers. These block copolymers have some miscibility with fatty acids and form mechanically stable thermoplastic elastomer gels (TPEGs) when mixed. Thermoplastic elastomer gel systems have been extensively studied;\textsuperscript{11} we will offer a brief discussion of their thermodynamics and precedent as phase change materials.

**Thermoplastic Elastomer Gels**
There are a large array of chemistries and morphological characteristics of block copolymers. When block copolymers are able to be modified with a midblock-selective solvent, the solvent can broadly tune the mechanical response of the overall network. A common model TPEG system is poly(styrene-b-ethylene-co-butylene-b-styrene) copolymer mixed with an aliphatic oil (e.g. mineral oil or squalane). In these TPEG systems with a low viscosity liquid solvent, softness is tunable based on volume fractions of solvent to polymer over a couple orders of magnitude (from approximately the kPa-MPa range). When the solvent has additional properties of interest, additional complexity can be added in the mechanical, thermal or electrical properties of the TPEG. These types of systems have been modified to include crystallizing solvents such as polydisperse\textsuperscript{12} and monodisperse\textsuperscript{13} paraffin waxes as PCMs. The PCM has drastically different mechanical properties in the solid (E: O~GPa) and liquid states ($\mu$: O~Pa$s^{-1}$) resulting a thermally switchable TPEG. Below the solvent transition temperature, crystalline hard segments dominate mechanical behavior, though the block copolymer network reinforces the structure thus increasing toughness; above the transition temperature, the block copolymer network dominates mechanical behavior.

**Materials and Methods:**

Phase change materials were formulated using a thermoplastic elastomer system: a commercially available thermoplastic copolyester (TcPE) developed by Eastman Chemical Company, trade name Ecdel production grades 9965, 9966 and 9967. These grades will further be described using the designations TcPE9965, TcPE9966 and TcPE-9967. The physical and thermal properties of all polymer grades are described in Table 7.1.
Fatty acids were used as a gellator and phase change component. The fatty acids were two fatty acid mixtures purified and distributed by Eastman Chemical Company under the trade names Pamolyn 100 and Pamolyn 200. Both grades are composed of 18 carbon fatty acids with variation in degree of unsaturation, i.e. oleic acid contains one unsaturation that can occur in two locations along the chain (either 9’ or 12’ carbon), and linoleic acid contains two unsaturations at the 9’ and 12’ carbons. Technical data on the two components is listed in Table 7.2. For simplicity, Pamolyn 100 and 200 will be referred to as oleic acid (OA, approximately 89%) and linoleic acid (LA approximately 74%) respectively throughout this document even though both are mixtures of oleic and linoleic acid along with small fractions of other fatty acids present. These fatty acids are useful for industrial application due to the prohibitive cost of separating fatty acids of similar molecular weight to a high degree of purity.

Gels were formulated using a melt mixing process (solvent free). The melting points of all grades of Ecdel were relatively similar (Figure 7.1a), and therefore a universal process was developed for use across all grades. Because the melting point of TcPEs is relatively high (~200 °C) and unsaturated fatty acids begin to oxidize rapidly at elevated temperature, there is a relatively small temperature window in which melt mixing can occur in oxygenated atmospheric conditions. All TcPEs were melted at 220 °C until transparent. Fatty acid was added to the molten polymer and mixed vigorously for no longer than 10 minutes using a mechanical mixer. Fatty acid was soluble in TcPEs to approximately 70 weight percent; macrophase separation was immediately evident at compositions of 80% fatty acid by weight and higher.
The oxidation of fatty acids during processing was of particular concern due to the potential of affecting phase change performance. Oxidation products may have reduced enthalpy of fusion or may not crystallize entirely. Oxidation products will also exhibit a change in miscibility with the thermoplastic elastomer matrix. For consistency in thermal measurements, it was necessary to account for thermal oxidation and use a correction factor based on thermal exposure time and temperature. Figure 7.1a shows measured enthalpy of fusion ($\Delta H$) of Pamolyn 100 throughout the oxidation process at 195°C. A first order reaction kinetic model of the form

$$f = \frac{\Delta H(t)}{\Delta H^*} = \frac{Ae^{-kt}}{A_0}$$

Eqn. 7.1

was used to fit the data and develop a correlation factor for thermal degradation during processing. The correction factor, $f$, is a ratio of enthalpy of fusion as a function of exposure time to the enthalpy of fusion before exposure, $\Delta H^* = \Delta H(t)$. Likewise, $A$, is an Arrhenius coefficient (i.e. temperature dependent) and $k$ is a rate constant. At 195°C $k = 2.55 \times 10^{-3}$ and $A = 118$. Figure 7.1b shows an image of OA following exposure to air at 195°C at varying exposure times corresponding to the enthalpy measurements in Figure 7.1a. In a production environment, it is believed necessary to add an antioxidant or oxygen free environment to protect against thermal degradation as the process times that show significant loss in enthalpy are relatively small, on the order of minutes.

Characterization of the thermal properties of fatty acids, thermoplastic elastomers and form-stable gels were done using TA Q100 (N2 gas cooled) and TA Q2000 (liquid N2 cooled) differential scanning calorimeters. All scans started at 40 °C and were run as cool/heat cycles
for multiple repeats. Tensile characterization was performed using an Instron (Model 5943) tensile stretcher. Thermal conductivity measurements were performed by melt casting form stable phase change gels between aluminum foil plates and pressing at 180 °C. Thermal conductivity of TcPE gels was measured using a Thermo Labo KES-F7 thermal conductivity testing apparatus. The thermal conductivity at 30% and at 60% fatty acid (Pamolyn 100) by weight was measured to be $0.17 \pm 0.05$ and $0.16 \pm 0.01$ W m$^{-1}$ K$^{-1}$ respectively. The thermal conductivity of the pure TcPE is $0.19$ W m$^{-1}$ K$^{-1}$ suggesting that the fatty acid addition does not significantly change the thermal conductivity.

**Mechanics.** Gels using TcPE as a network former were studied over a broad range of compositions with the peak miscibility limit ending at approximately 70 weight percent on a mass basis for oleic and linoleic acid in each elastomer grade. Above 70 weight percent, fatty acid is not tightly bound to the elastomer matrix and the surface of the gel appears wet, draining over time to an equilibrium concentration. To understand how well bound fatty acid is to the elastomer matrix, an exusion test was performed at room temperature on a TcPE-OA-40 gel. Figure 7.2 shows the results of the exusion test on a gel mass basis and a fatty acid mass basis. At low pressures, the fatty acid is tightly bound enough for the gel to retain most of the acid. Extremely high pressures will cause significant leakage of the phase change solvent.

Very distinct changes in mechanical properties were noted through fatty acid addition to TcPE grades with minor variation as a function of elastomer grade. Figure 7.3 shows mechanical extention tests of TcPE 9965-OA-25 (25 wt% oleic acid) compared to a neat TcPE copolymer. Tensile strength and toughness are drastically reduced with the addition of solvent, but solid-like behavior is clearly maintained. This likely indicates a disruption of physical
crosslink formations due to either 1) increased spacing between crosslinks and decreased bridging from short polyol connecting chain lengths, or 2) some solubility of fatty acid in the crystalline segments of the TcPE that disrupts crystal formation or adds crystalline defects. Solid-like behavior with weakened mechanics continues to approximately 50 weight percent TcPE; at greater than 50 percent fatty acid, the gel begins to take on liquid-like properties being easily spreadable in the liquid gel state, though the gel will not flow under its own weight.

**Melting point variation.** Melting point variation was loosely if at all correlated to TcPE gel composition. Variations are attributed to broad melting and crystallization peaks rather than true variations in melting point. Figure 7.4a shows the melting and crystallization temperatures of TcPE9965-OA gels as a function of fatty acid composition at both the onset and the peak of the 1st order phase change. Figure 7.4b shows a slight dependence of phase transition temperature on composition of linoleic acid, but again, the effect is small and we are not confident in attributing the dependence to a true variation in melting point. The peak breadth for crystallization and melting typically span ~10°C and ~20°C respectively for Pamolyn 100 and Pamolyn 200.

The DSC traces of each gel (Figure 7.5) are of particular interest specifically in the differences between PCM gels and fatty acid PCMs with no network forming additive. Figure 7.5a shows six overlaid, highly repeatable DSC traces of TcPE 9965-OA-60. Comparatively, Figure 7.5b shows the DSC trace of pure OA. While the oleic acid peaks in each specimen differ only in magnitude of enthalpy, there are distinct differences in the shape of the melting peak associated with linoleic acid, suggesting a difference in phase behavior due to a network related interaction.14
**Enthalpy.** Enthalpy associated with phase change is of primary importance for PCMs. Organic PCMs should demonstrate a high enthalpy of fusion to mass and volume ratio to be effective in energy storage and temperature regulation applications. Figure 7.6a focuses on TcPE9965-OA enthalpy of fusion as a function of composition. Note that reported enthalpies include all melting and crystallization peaks associated with oleic acid as well as linoleic acid. This is due to the difficulty in discerning which peaks are associated to corresponding fatty acids as their gel fraction increases and peaks broaden and overlap. This can give an integration range of >30°C, though the majority of latent energy transfer during melting occurs between ~5°C and ~15°C in all cases for Pamolyn 100 based gels. The peak broadening with variation in fatty acid concentration is demonstrated in Figure 7.7.

Figure 7.6b shows the melting enthalpies of TcPE (9965, 9966 and 9967) as a comparison between grades. The highest molecular weight grade (9967) demonstrates a consistent trend relating melting enthalpy to fatty acid composition, but both the 9965 and 9966 grades demonstrated a deviation from the expected latent heat of fusion. While not completely understood, possible explanations will be discussed further.

**Discussion**

The real attraction for thermoplastic elastomer gel based PCMs lies in the straightforward processing methods that are potentially available. Injection molding, calendaring, fiber production and many other traditional polymer processing methods are all conceivable. Additionally, the possibility of producing layered composites and protective film coatings on these form-stable PCMs is available. Compared to the complex process of encapsulation used in other commercial PCMs, a direct mixing process of a thermoplastic
elastomer gel and PCM is highly preferable. Microencapsulation is estimated to make up 45-65% of the total cost of the PCM.\textsuperscript{16}

We found it of importance to investigate a commercially available thermoplastic elastomer as a network former as well as a commercially available phase change material to study some of the realistic concerns associated with existing polymer chemistry and architecture and low purity PCMs. Some of these concerns include the use of low purity PCMs and mixtures of PCMs, co-crystallization of PCMs, the importance of TPE architecture (especially block length), and the viability of fatty acids as PCMs that have lower enthalpy of fusion than linear hydrocarbon PCMs. These materials provide a practical route to a commercial form-stable PCM at relatively low cost, but understanding the effects of non-ideal purity and polymer architecture are imperative for form-stable PCMs.

First, the importance of using mixtures of fatty acids cannot be understated. Fatty acids are primarily purified by chromatographic methods,\textsuperscript{17} which is often rather costly, and minimizing columns in processing can save on production costs. Still, fatty acids are relatively cheap compared to paraffins and inorganic PCMs\textsuperscript{18,19} and are produced from biofeedstocks. A broad range of melting points are accessible with fatty acid based PCMs as there are many naturally occurring chain lengths and degrees of saturation. Additionally, forming eutectic mixtures of fatty acids with different melting points can produce unique melting points for a highly tailorable PCM system.

Non-eutectic mixtures will have more than one type of crystalline population with distinct melting points and enthalpies. Multiple melting temperatures are present in both the OA and LA fatty acids (Figure 7.5). The eutectic point of oleic and linoleic acid mixtures lies
between 75.2% and 76.3% (molar basis) linoleic acid (depending on the α or β form of oleic acid) at a temperature of approximately -10°C.\textsuperscript{20} The OA used in this study is far from the eutectic point, but the LA is near the eutectic point, explaining the single peak from DSC traces. The measured melting temperature is significantly lower than reported values of eutectic oleic-linoleic mixtures.

The melting temperatures of thermoplastic elastomer gels remain constant for both phase change fatty acid mixtures implying little interference of the polymer network with the crystalline structure or crystallite size. There are small secondary peaks observed for linoleic acid (Figure 7.5c) that are only present in the gels, but the temperature shift is relatively small. It is possible that there is a partitioning of fatty acids to different block copolymer phase domains within the gel that causes this change. This could account for the reduction in mechanical strength (due to disruption of crystallization of the TcPE) as well as the splitting of melting peaks in DSC traces. Figure 7.7 shows melting curves of TcPE 9967-OA at varying weight fractions, and there is a pronounced decrease and shift in the secondary peaks.

The deviation from expected enthalpy of melting shown at low OA fatty acid fractions in Figure 7.6 is a puzzling feature. The total sum of enthalpy of fusion of both oleic acid and linoleic acid rich phases is 148 J/g (literature values of $\Delta H$ for oleic acid are 140 J/g)\textsuperscript{21} and the expected enthalpy of fusion of each gel, $\Delta H_{gel}$, is calculated (dotted line Figure 6) as simply

$$\Delta H_{gel} = w_{OA}\Delta H^*$$

Eqn. 7.2

where $w_{OA}$ is the weight fraction of OA. There is a possibility that crystallization is frustrated by a high concentration of amorphous polymer chains from the TcPE network, but as shown by the DSC curves in Figure 6.7, there appears to be deviation from baseline heat flow that
spans the entire range of the first melting peak to the primary oleic acid rich phase melting peak (a range of over 30°C). Integrating over the entire range of -20 to 20°C on the DSC traces gives results shown in Figure 6.6b. There is still a deviation from ideal at low weight fractions even when accounting for all the enthalpic peaks.

The TcPE based gel with a fatty acid PCM shows great promise as a low cost form-stable PCM for applications in building materials, films and coatings for thermal energy management. While fatty acids have a lower enthalpy of fusion than paraffins, they are generally cheaper to manufacture and they offer a high degree of tunability in melting point. Figure 7.8 compares the performance of the TcPE elastomer gels to that of a commercial microencapsulated paraffin. The results are extremely promising and cost considerations suggest a form stable PCM to be much more effective on a per dollar basis than paraffin based PCMs. The high loading of fatty acid into form-stable TcPE matrix makes this gel competitive to encapsulated PCMs that will necessarily have lower loading. Additionally, specific tailoring of the TcPE properties for longer block lengths will likely improve loading capacity of fatty acids. The processing possibilities of TcPE-fatty acid PCMs are again a major benefit to the system as well, especially considering the potential for composite materials to improve mechanics, thermal conductivity and thermal resistance.
Table 7.1. Material Properties of Copolyesters

<table>
<thead>
<tr>
<th>Polymer Grade (Trade Name Ecdel)</th>
<th>Melting Point (°C)</th>
<th>Heat of Fusion (J/g)</th>
<th>Thermal Conductivity (Wm⁻¹K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9965</td>
<td>207</td>
<td>27</td>
<td>0.19</td>
</tr>
<tr>
<td>9966</td>
<td>205</td>
<td>27</td>
<td>0.19</td>
</tr>
<tr>
<td>9967</td>
<td>205</td>
<td>27</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Table 7.2. Material Properties of Fatty Acid Mixtures

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Oleic Acid** (mol %)</th>
<th>Linoleic Acid (mol %)</th>
<th>Melting Point (°C)</th>
<th>Crystallization Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pamolyn 100</td>
<td>89</td>
<td>7</td>
<td>11</td>
<td>-1</td>
</tr>
<tr>
<td>Pamolyn 200</td>
<td>74</td>
<td>20</td>
<td>-18</td>
<td>-34</td>
</tr>
</tbody>
</table>

**Note: mole fractions of oleic and linoleic do not sum to unity because of the presence of other fatty acids in small quantities (< 4%) and unsaponifiable organics.
Figure 7.1. A) Crystallization and melting enthalpies of oleic acid following thermal exposure. A first order exponential fit is used as a model assuming a first order oxidation reaction, but is not meant to be mechanistically representative. B) Discoloration of oleic acid (Pamolyn 100) after thermal exposure in oxygenated atmosphere at 195°C.
Figure 7.2. Results of a solvent exusion test conducted on a hydraulic press. Solid mass fractions are measured after successive application of pressure. Pressures are given in metric tons/16 in$^2$. The black curve represents total remaining mass fraction on a gel basis and the blue curve represents remaining mass of fatty acid based on the initial fatty acid mass within the form stable gel.
Figure 7.3. Quasi-static tensile extension tests of TcPE 9965 with no fatty acid additive compared to 9965-O-25. The tensile modulus changes from 106.8 MPa to 9.33 MPa with the addition of fatty acid (Pamolyn 100). The inset shows the drastic decrease in strength and toughness upon the addition of fatty acid that swells short amorphous chains.
Figure 7.4. A) Melting temperatures of TcPE-9965 with oleic acid (Pamolyn 100) over a range of compositions. Dotted lines indicate the average melting temperatures over the entire range of compositions as there is no significant deviation in melting temperature. B) Melting temperatures of TcPE-9965 with linoleic acid (Pamolyn 200). There appears to be a slight dependence of melting and crystallization point on composition.
Figure 7.5. A) Melting and Crystallization of TcPE9965-OA-60 showing 6 consecutive heating and cooling cycles. A point of note is the disrupted melting peak of the linoleic acid rich phase which consistently B) A single DSC trace of OA showing two distinct melting peaks for an oleic acid rich phase at ~0°C and a linoleic acid rich phase at ~20°C. C) DSC curves of LA and 50 weight percent mixtures of TcPE and LA with grades labeled on the plot. Heat flow is given in arbitrary units.
Figure 7.6. A) Enthalpy of Crystallization of TcPE 9965 as a function of composition considering only the primary peak (i.e. over a temperature range of ~0 to 20°C. Crystallization integrations are shown in blue and melting integrations shown in red. B) Comparison of the enthalpy of fusion (melting) of 9965 (●), 9966 (●) and 9967 (●) TcPEs as a function of oleic acid fraction considering all enthalpic melting peaks over a range of approximately -20 to 20°C.
Figure 7.7. Traces from DSC of TcPE 9967 gels of varying mass fraction label on the plot. The secondary peak (linoleic acid rich phase) gradually spreads out over a large temperature range.
Figure 7.8. A) Comparison of TcPE based form-stable PCM to a commercial microencapsulated product. B) The suggested loading for applications of microencapsulated paraffin PCM are ~40% by volume, whereas the TcPE form-stable PCM can be used at a 70% loading. This comparison gives a more realistic enthalpy of fusion for PCMs used for energy management or energy storage applications.
References


8 Future Work

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This work has produced a number of ideas that were not entirely realized. The following chapter highlights some of the better ideas that have been explored for dielectric elastomers (DEs) as actuators but require further study.

8.1 Novel TPEG for Prestrain-free Dielectric Elastomer.

In the DE community, a handful of materials have shouldered the weight of the entire field. The vast majority of work in the field has been conducted using chemically cross-linked silicone and acrylic elastomers, especially 3M’s VHB acrylic tape. Until recently, only a small group of researchers within the field have attempted to explore alternative options and design elastomers for specific applications as DEs. More recently, investigations into polymer blends and composites have been explored more thoroughly, especially conductive carbon species as fillers.\(^1\) Although some aspects of DE performance have been improved beyond VHB, \(e.g\). electromechanical coupling\(^2\) and dielectric constant,\(^3,4\) there have only recently been breakthroughs that clearly justify a new archetype material to replace VHB.\(^5\) It was over a decade before rationally designed elastomers successfully outperformed VHB in the metrics of actuation strain, energy density and the potential for prestrain-free actuation.\(^6\) These acrylic elastomers have been proven as exceptional DE materials due to their molecular polarizability and desirable mechanical attributes. This proposal focuses on improving acrylic TPEGs by modifying the chemistry of the TPE and the selective solvent.

A previous implementation of acrylic TPEGs\(^6\) has shown incredible actuation results, but there are some issues associated with the design. First, the midblock selective solvent
(dioctyl phthalate) is a toxic substance not suitable for use in applications involving human contact. Additionally, the chemical similarity of the end blocks and midblock of the TPE make physical crosslinks susceptible to plasticization by nearly any solvent intended to be selective for midblock miscibility. Continuing the work on polar TPEGs, I propose the use of an elastomeric copolymer with highly incompatible blocks. In order to make predictions about the electromechanical behavior of this type of TPEG, poly[styrene-\(b\)-n-butyl acrylate-\(b\)- styrene] (SnBAS) will be a model material. This material will provide advantages over all-acrylic TPEGs by allowing for a broad selection of extremely polar mid-block selective solvents with high permittivity.

There has been active interest in developing styrene/acrylic elastomers with enhanced functionality over the traditional synthetic rubbers such as SEBS, SBS, SIS, etc. In particular, there have been multiple efforts to synthesize poly(styrene-\(b\)-n-butyl acrylate-\(b\)-styrene) (SnBAS) triblocks which are not easily synthesized via anionic living polymerization due to the propensity for acrylics to suffer greatly from bite-back termination. Because of this limitation, polymerization reactions are low temperature (therefore slow, as well as requiring cost-ineffective reactor heat duties), polydisperse and outright challenging. This makes synthesis of SnBAS elastomer economically unattractive, even if they offer some mechanically and chemically superior properties.

Other controlled living radical polymerizations (CLRPs) have been explored more recently including atom transfer radical polymerization,\(^7\) nitroxide mediated polymerization,\(^8\) and most successfully reversible addition-fragmentation chain-transfer polymerization.\(^9\) Luo et al. have synthesized a series of triblock copolymers (SnBAS) in an emulsion polymerization
with remarkable mechanical properties—with elongation at break up to 1300% and modulus of 0.22 MPa for a particular specimen (approximately 30k-240k-30k). This shows the potential for hyperelastic behavior on par with SEBS elastomers at a lower modulus and comparable toughness (two properties of particular interest for effective dielectric elastomers). With continuing advances in CLRP methods, commercially available TPEs with extremely high incompatibility and chemical dissimilarity are becoming commercially viable.

Increasing permittivity of a DE provides a number of advantages in regard to performance. The conceivable actuation strains and energy density become much larger as permittivity increases, but the actuation behavior of dielectric elastomers depends on multiple material parameters. Elastomeric composites containing stiff fillers show decreased mechanical strength and increased modulus—both poor DEA attributes. Such materials have been investigated, and while there is an observed increase in permittivity, the net effect is detrimental. Additionally, high permittivity components tend to have high dielectric losses that can ultimately reduce the breakdown strength of the DE. Figure 8.1 shows a comparison of some simple models: the Maxwell-Wagner model for dielectric composites (Equation 8.1) and a shear modulus model that predict the real portion of the permittivity and the shear modulus of a composite elastomer. A soft additive with high permittivity could make substantial improvements in electroactuation.

Here the use of liquids with high permittivity is proposed to bypass some of the issues associated with stiff fillers. Liquid plasticizers are capable of enhancing film permittivity and potentially decreasing the stiffness. There are a number of conceivable methods for incorporating high dielectric constant liquids into an elastomer including formation of elastic
gels, dispersed liquid droplets, etc. Thus far, the use of liquids as dielectrics has not been investigated in great detail. Because the dielectric constant of the most prevalent DEA materials (3M VHB 4910 and HS Silicone) are relatively low, even small improvements in permittivity could potentially revolutionize the standard for DEA materials. Additionally, large fractions of high permittivity material (approaching 95 weight percent in the instance of TPEGs) can be incorporated into an elastomer without adverse effects in mechanical properties.

To make TPEGs for DE applications from SnBAS triblocks, high dielectric constant solvents such as propylene carbonate and ethylene carbonate ($\epsilon' = 64$ and $\epsilon' = 93$ at 30°C, respectively) are compatible with acrylates. Both solvents are biocompatible and FDA approved for topical use. Additionally, both have low volatility and are low cost. Considering designs modeled after SEBS/MO TPEG DEs, one can imagine a TPEG with as low as 5 wt% copolymer and a dielectric constant an order of magnitude greater than any non-composite DE in the literature to date. The Maxwell-Wagner dielectric composite model predictions for SnBAS gels are shown in Figure 8.2. The Maxwell-Wagner Model is defined by

$$\epsilon_c = \epsilon_2 \left[1 - 2\phi \left(\frac{\epsilon_2 - \epsilon_1}{(2\epsilon_2 + \epsilon_1)}\right)\right]/\left[1 + \phi \left(\frac{\epsilon_2 - \epsilon_1}{(2\epsilon_2 + \epsilon_1)}\right)\right]$$

Eqn. 8.1

where ‘2’ indicates the matrix, and ‘1’ indicates the filler. In this case, microphase domains of polystyrene blocks are taken to be the filler ($\epsilon_1 = 2.1$) and the solvated blocks of poly(ethyl acrylate) are taken to be the matrix.

Based on these predictions, we believe it would be possible to synthesize a number of block copolymer systems. In order to employ interchangeable monomer chemistry, it is proposed that a macromonomer process is used with acrylate capped polystyrene. The
architecture of the resulting block copolymers is similar to that of a low density brush with polystyrene macromonomers polymerized with the main chain monomer. The resulting polymer architecture is shown in Figure 8.3a. Monomers of interest as a main chain are: n-butyl acrylate, methacrylate, methyl methacrylate or acrylonitrile. The proposed synthesis scheme is shown in Figure 8.3b.

We find it of interest to include glassy polymers ($T_g > 25^\circ C$) as potential main chain candidates due to the possibility of shape memory applications.\textsuperscript{13,14} Using TPEGs, the amount of solvent present in the gel can be used to tune the glass transition temperature according to straightforward mixing rules of single phase polymer-solvent systems.\textsuperscript{15} For example, a copolymer of PMMA with a mass fraction of 0.71-0.83 would yield a shape memory TPEG with propylene carbonate selective solvent with a $T_g$ between $0^\circ C$ and $40^\circ C$ while the styrene block $T_g$ would remain $\sim 100^\circ C$. This material would provide the advantage of rapid transitions relative to crystallization (1\textsuperscript{st} order phase transition), higher dielectric constant and blocking stress.

### 8.2 High Dielectric Constant Acrylamide Gel Fibers for Anisotropic Dielectric Elastomers

The most common applications of DEs involve actuation mechanisms that take advantage of the areal expansion of a DE film. Examples of this are seen in actuator designs such as diaphragm actuators\textsuperscript{16–18} and minimum free energy structures.\textsuperscript{19,20} In order to use DEs in a mechanism truly meeting the definition of biomimicry, linear actuations are necessary. Stack DE actuators can be used to perform linear actuations by utilizing transverse strain, but their fabrication is complex and, due to the thin film nature of DEs, actuation displacements in
transverse actuation are small. Rather, the use of DEs with inherent mechanical anisotropy to perform anisotropic area expansion are more desirable. This has been accomplished by oriented carbon fiber electrodes,\textsuperscript{21} anisotropic prestreches\textsuperscript{22} and the addition of aligned fibers in a DE actuators.\textsuperscript{4}

The use of aligned fibers that have substantially different mechanical properties, has shown that actuations can be made highly anisotropic. Some effort was taken to decouple the mechanical effects from the electrical ones. Here, we intended to explore the effects of combining TPEGs (SEBS/MO) with high dielectric constant materials in composites to improve the dielectric constant without drastically changing the mechanical properties of the elastomer material. The high dielectric material of interest is a chemically crosslinked acrylamide gel with Glycerol ($\varepsilon \approx$42) as a swelling solvent. Glycerol has a boiling point of 290°C, making it stable at room temperature.

Synthesis of the acrylamide films is based on a highly stretchable acrylamide (Aam) hydrogel described by Bai et al.\textsuperscript{23,24} The synthesis is done via an aqueous photopolymerization with 2,2-dimethoxy-2-phenylacetophenone as the initiator and methylene $bis$-acylamide as a crosslinker. Monomer concentration of the pre-polymer solution is 2.2 molar with concentrations of 0.17% and 0.06% by weight with respect to acrylamide monomer, respectively. This yields a highly stretchable aqueous acrylamide gel with a tensile modulus of 7.4 kPa and extension at break of ~300%. Films are formed by conducting the polymerization between glass slides with a 1 mm or 0.5 mm spacer. A solvent exchange is done post-polymerization to replace water with glycerol by adding a glycerol/water solution (1:1 volume ratio) to the polymerization vessel. The polymer swells to absorb all of the additional solvent.
and is then dried in a 60°C oven for 1 day to remove water. The fraction of glycerol in the resulting hydrogel is approximately 86%.

The composites were made in two methods: 1) a layered composite for isotropic actuation, and 2) a “fiber” based anisotropic DEA. In the layered composite, SEBS/MO elastomer acts primarily as a passivating layer to prevent current flow to the Aam/Glycerol film that is capable of solubilizing high concentrations of ionic species. The layered composite is approximately 1.6 mm in total thickness (two 300 micron films of SEBS/MO TPEG and a 1 mm thick film of Aam/Glycerol). Figure 8.4a shows a cross-section schematic of the DE with an overhead image of the DE in Figure 8.4b. Electroactuation strains are limited to relatively small area actuations of ~8% before dielectric breakdown, but these strains occur at extremely low electric fields of 0-3 kV/mm, showing promise for their potential use.

The fiber based composites use a laser writer to cut ~300 micron strips of acrylamide gel to be sandwiched between layers of SEBS/MO elastomer (10/90 weight percent respectively). The compressive moduli of the Aam and the SEBS based gels are on the same order of magnitude. Layers of SEBS/MO gel were thermally welded together to sandwich acrylamide fibers into a composite structure. The films are equibiaxially prestrained 300% prior to actuation experiments. Figure 8.5a shows the actuation behavior of an Aam/Glycerol composite compared to a SEBS/MO gel. The two DE actuators show drastically different actuation trends. The composite material shows an electric field dependence proportional to $E^{-1}$ rather than the expected dependence of $E^2$.

While these systems show promise, a great degree of characterization is necessary to optimize their actuation behavior and understand the mechanisms governing actuation. The
strange trend in actuation strain of layered composites of fiber Aam/Glycerol composites is not understood, and the development of an underlying theory is necessary.

8.3 Ternary Styrenic Thermoplastic Elastomer Gels with Increased Permittivity Solvents

We have preliminarily investigated a novel TPEG that incorporates a midblock selective solvent with enhanced permittivity. Specifically, the solvent is a high permittivity oligomer that is mineral oil soluble and can be compatibilized into the midblock. This ternary gel exhibits mechanical properties comparable to the previously explored TPEG systems containing SEBS and mineral oil. The first system is a ternary polymer gel composed of a triblock copolymer (SEBS), an oil soluble poly(alkylene glycol) oligomer (OSP), poly(butylene glycol-co-propylene glycol), and a white mineral oil to compatibilize the two other components. Both the mineral oil and PAG are expected to act as midblock selective solvents. The OSP is a commercially available lubricant manufactured by DOW (trade name OSP-32, where the trailing numbers indicate viscosity). It is specifically designed to be soluble in mineral oils, but the oligomers are not only partially miscible in elastic polymers. Because of this, the PAG used here is low molecular weight (~1000 Da) to promote both elastomer swelling and high dielectric constant. The oligomer is synthesized via a copolymerization of epoxy propylene and epoxy butylene. Future plans for this work involve the synthesis of PBO oligomers to improve miscibility between PAG and elastomer. Because the miscibility of the OSP is dependent on the composition of the copolymer, oligomers with increased miscibility can be synthesized with minor changes in reaction chemistry. The use of higher alkylene oxide monomers will be investigated in future work.

Oligomers composed of poly(butylene glycol) and higher PAGs such as poly(propylene glycol monobutyl ether) are expected to be miscible with the ethylene-co-butylene midblocks of the SEBS TPE based on experimental evidence. A phase diagram summarizing the macroscopic
miscibility of these ternary systems is shown in Figure 8.6. Miscibility has been determined by optical clarity and solvent retention. The miscibility of this particular grade of OSP is limited to approximately 20 weight percent OSP, but surprisingly, miscibility of the OSP appears to decrease slightly with decreasing TPE composition. This result requires a more in depth analysis to understand, but because of the unknown and somewhat arbitrary composition of this particular OSP copolymer, it has been deemed unnecessary.

By using higher alkylene oxide repeat units, miscibility increases, but the overall polarity of the repeat unit is decreased. This trade off should be considered in order to optimize both the loading and polarity of OSP in order to maximize permittivity. Oxygen atoms on the on backbone of OSP oligomers provide permanent dipole moments along the chain. Permanent dipoles are sensitive to polarization at the molecular level in low frequency electric fields, and polar organic molecules tend to have high permittivity for this reason. Sengwa et al.\textsuperscript{26} have shown that short chains of poly(ethylene glycol) have high dielectric constant due to polar moieties and the rotational flexibility of the backbone, and the dielectric constant increases drastically with decreasing molecular weight. Measurements of the dielectric constant of a ternary gel were taken using an Agilent 4284A impedance analyzer (Figure 8.7).

The TPEGs were solution cast in toluene at room temperature. Ternary gels consisted of three components: SEBS triblock copolymer (Kraton G1654, $M_n=144$ kDa, 30% styrene by volume), white mineral oil (Sonneborne, Hydrobrite 380 PO), and oil-soluble polyalkylene glycol (DOW, OSP-32, $M_n=1.0$ kDa). Predetermined weight ratios of each component were combined and diluted to 5 percent copolymer (w/v). Gels were allowed to cast over 96 hours to ensure solvent evaporation and diffusion to the surface occurred on the same time scale, and uniform films were formed. Gels were annealed under vacuum (~25 Torr) at 140°C for 8-16 hours to ensure removal
of residual solvent. Films for dielectric elastomers were melt pressed into 50x50x0.53 mm³ templates at 180°C and quench cooled.

Electroactuation tests were performed by painting circular electrodes onto unstrained TPEG films with a conductive grease (Nyogel 753G, Nye Lubricants). Figure 8.8 shows the electroactuation strains of prestrain-free DEs containing 20% OSP at copolymer concentrations of 15, 20 and 25%. Maximum actuation strains range from 11% to 26% by area and are achieved at lower electric field strengths than comparable prestrain-free SEBS/MO TPEGs. Electrical fields were generated using a Gamma High Voltage ES 30 kV power source. Actuation was measured using digital images and image analysis software (ImageJ) employing an in-house script for pixel counting to ensure accurate measurements.

Prestrain-free DE actuators incorporating 20 weight percent OSP showed improved performance over similar SEBS TPEGs without PAG. Electromechanical coupling efficiency was calculated be up to 0.356. Low electric fields are required for actuation, proving the efficacy of using solvents with high dielectric constant, but further tailoring of the mechanical properties is required to improve the actuation strain. Prestrain-free DE actuators exhibit smaller actuation strains than biaxially prestrained DEs. Mostly, this is due to a drastic increase in the dielectric breakdown strength that accompanies prestraining. For example, SEBS has a breakdown strength of approximately 30 kV/mm in an unstrained state, but is capable of withstanding fields greater than 100 kV/mm when equi-biaxially prestrained (λ₁=λ₂=3). Addition of high permittivity components presumably lowers the dielectric strength.

8.4 Conclusions

It is hoped that these ideas will be built upon in the future and explored more fully. The concept of high dielectric constant liquids as electroactive materials has been demonstrated by
others,\textsuperscript{27} but their use directly incorporated into a dielectric elastomer gel is still an unexplored avenue. Additionally, the importance of rationally designed polymers for dielectric elastomers is imperative to the success of the field. While many areas in the field including modelling\textsuperscript{28–30} and actuator design\textsuperscript{31,32} have been investigated vigorously, polymer scientists are needed to solve the problems associated with high voltage requirements and the elimination for the need to mechanically prestrain DEs. The high dielectric constant gels described here are promising candidates to produce next generation materials for DE actuators and generators.
Figure 8.1. (A) Material models of a composite dielectric material (PMN-PT particles in SEBS) are used to predict static dielectric constant (●) using the Maxwell-Wagner model and shear modulus\textsuperscript{33} (●), $G'$. (B) The normalized transverse strain coefficient ($\varepsilon_0\varepsilon'/G'$) is given as a function of filler volume fraction. It is evident that even in the best case of stiff fillers with a very large dielectric constant, such as PMN-PT, modest gains can be made in DE actuator improvement and those improvements come at the cost of decreased dielectric breakdown strength.
Figure 8.2. The Maxwell-Wagner composite model is used to predict the dielectric constant of TPEGs using SnBAS triblock copolymers and two carbonate solvents. The midblock is assumed to be miscible with the solvents and the endblocks completely immiscible.
Figure 8.3. (A) Model of proposed block copolymer architecture where blue beads represent polystyrene and red beads represent a polar repeat unit, specifically n-butyl acrylate, methacrylate, methyl methacrylate, ethylene oxide or acrylonitrile. The location of styrene chains is random, but the “graft” density is tunable through relative polymerization concentrations of polar monomer and polystyrene macromonomer. (B) Proposed synthesis of functionalized polystyrene macromonomer.
Figure 8.4. (A) Layered Hydrogel composite schematic with compliant electrodes applied to either side of a tri-layer composite: SEBS/MO-Aam/Glycerol-SEBS/MO. The SEBS/MO passivating layer is 15% polymer by weight. (B) Image of layered composite amphigel DE. (C) Transverse actuation strain of an amphigel layered composite elastomer to breakdown voltage.
Figure 8.5. (A) Areal actuation strain of biaxially prestrained SEBS elastomer and a SEBS/Aam composite. (B) Electromechanical anisotropy of fiber enforced SEBS/Aam composites.
Figure 8.6. The miscibility of ternary mixtures of SEBS-OSP-MO gels are shown.
Figure 8.7. The dielectric constant of three SEBS-based TPEGs are measured over a broad range of frequencies, (●) SEBS-OSP-MO (20/20/60 weight %, respectively) and (●) SEBS-MO (20/80 weight % respectively).
Figure 8.8. Electroactuation tests of ternary component gels (SEBS-OSP-MO) of varying copolymer and MO composition (OSP fixed at 20 weight percent). Addition of OSP decreases poling voltage when compared to SEBS-MO DEs, but also appears to decrease the dielectric breakdown strength—explaining the failure at low strain.


8. Robin, S., Guerret, O., Couturier, J., Pirri, R. & Gnanou, Y. Synthesis and


24. Chen, B. *et al.* Stretchable and transparent hydrogels as soft conductors for dielectric


Appendix A

Quasi-Solid-State Dye-Sensitized Solar Cells Containing a Charged Thermoplastic Elastomeric Gel Electrolyte and Hydrophilic/phobic Photosensitizers

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Abstract

As the threat of global climate change due to combustion emissions becomes increasingly alarming, the search for clean and sustainable alternative energy sources is of paramount importance. With this objective in mind, harnessing solar energy is particularly attractive due to ongoing improvements in silicon-, perovskite- and organic-based solar cells. Of these, dye-sensitized solar cells (DSSCs) remain a promising technology due to their relatively low cost, moderate conversion efficiency and robust mechanical properties. An important breakthrough in the development of DSSCs is the use of polymer gel electrolytes. In this work, we employ novel thermoplastic elastomers (TPEs) in the form of sulfonated block ionomer (SBI) homologues for this purpose. Since the midblock of each charged copolymer is

This appendix is a manuscript submitted to Sustainable Energy & Fuels that has been accepted; it is expected to be published in 2017.
amphiphilic, the resultant microphase-separated nanostructures are thermodynamically stable and consist of continuous ionic channels to expedite electron diffusion. A unique characteristic of the SBI archetype studied here is that the morphology can be solvent-templated. We exploit this feature by introducing either hydrophilic or hydrophobic photosensitizers into the DSSCs. When the SBI exhibits a lamellar morphology, a hydrophilic dye yields the highest efficiency (7.0%), whereas the opposite is observed when the nanostructure consists of a nonpolar matrix. Photosensitizer tunability is augmented by the intrinsic mechanical and adhesive properties of a typical TPE.

**Introduction**

In an era when emissions from petroleum-based fuel sources continue to come under scrutiny as a primary cause of global climate change, solar energy constitutes one of the most promising candidates for producing renewable and clean energy. Solar cells, or photovoltaics, are self-standing devices that transform light to electricity through the use of various materials, ranging from inorganic species such as silicon to hybrid organic-inorganic perovskites and polymer nanocomposites typically composed of a polythiophene in the presence of carbonaceous nanomaterials. Another avenue by which to harness solar energy relies on the use of dye-sensitized solar cells (DSSCs), which have been extensively studied since the seminal efforts of O'Regan and Grätzel in 1991. Unlike traditional silicon-based solar cells, DSSCs are able to function independent of incident light angle in low-light conditions as light sponges and, by doing so, are less susceptible to thermal energy loss. An important distinction of the classic DSSC is the incorporation of mesoporous titanium dioxide (TiO₂). After a photosensitive dye molecule in a DSSC absorbs an energetic photon during light
harvesting, an electron in a photosensitizer hops from its ground state to its first excited singlet state. Photosensitizer oxidation occurs when such electrons, injected into the conduction band edge of the mesoporous TiO$_2$ layer, are transported from the anode and flow through a load to the cathode. There, they are re-introduced into the cell through a redox mediator to replenish the hole generated in the dye so that the dye can harvest another photon and repeat the oxidation-reduction process. Thus, in addition to the presence of TiO$_2$, judicious choices of electrodes, dye and electrolyte are crucial to the production of energy-efficient DSSCs.$^{15,16}$ Relative to their inorganic analogs, this promising class of photovoltaics is generally fabricated from materials that are non-toxic, environmentally friendly and low-cost. While many DSSC designs employ liquid electrolytes as the contiguous electron-transfer medium, this strategy possesses major drawbacks, including solvent leakage, corrosion and evaporation, which together affect the stability of the DSSC.$^{15,17-19}$ An alternative strategy introduces solid- or quasi-solid-state electrolytes.$^{20-22}$

Block copolymers (BCPs) are suitable for use in both solid- and quasi-solid-state DSSCs. An important characteristic of BCPs is their ability to spontaneously self-assemble into a variety of nanoscale morphologies due to thermodynamic incompatibility between the constituent blocks.$^{23,24}$ Classic morphologies of bicomponent (A-B type) block copolymers include spherical A(B) micelles positioned on a body- or face-centered-cubic lattice in a B(A) matrix, A(B) cylinders arranged on a hexagonal lattice in a B(A) matrix and alternating lamellae. More spatially complex morphologies, such as the gyroid,$^{25,26}$ bicontinuous microemulsions$^{27}$ and coexisting nanostructures,$^{28}$ have been found to form in neat block copolymers, as well as in their blends with liquid diluents$^{29,30}$ and other copolymers.$^{31,32}$
some of these morphologies, a conductive matrix or contiguous conductive pathways naturally facilitates the diffusion of electrons to the working electrode, where they can be efficiently collected by the counter electrode. In the presence of a block-selective liquid, a BCP can serve to adjust the viscosity of the liquid or, at sufficiently high concentrations, retain a distinctive nanostructure and gel (that is, solidify) the liquid if the BCP is able to form a molecular network (as in the case of thermoplastic elastomer gels). Room-temperature ionic liquids (RTILs), organic salts exhibiting low melting temperatures and low (if any) vapor pressure, are of particular interest in DSSCs as replacements for flammable organic solvents. Addition of small quantities of a BCP to RTILs increases liquid viscosity and, above the critical gel concentration, promotes the formation of a gel that can exhibit solid-like mechanical properties, depending on the BCP and its concentration. For example, DSSCs containing quasi-solid ion-gel electrolytes have been fabricated from 1-propyl-3-methyl imidazolium iodide with a small amount of a poly(styrene-b-ethylene oxide-b-styrene) (SEOS) triblock copolymer. The added BCP increases efficiency and maintains 92% of its initial efficiency after more than 1440 h of operation, but lowers the redox mediator diffusion. As a potential drawback, excess BCP hinders deep penetration of the electrolyte into the mesoporous TiO$_2$.

Another approach by which to eliminate complications associated with liquid electrolytes through the inclusion of a BCP is to generate a quasi-solid-state (QS) electrolyte. Dong et al. have explored the efficacy of a poly(ethylene oxide-b-amide-imide) BCP to form physically cross-linked gels intended to absorb a liquid electrolyte and form a nanochannel network wherein the BCP serves as the matrix of a polymer gel electrolyte (PGE). In this case,
the PGE imbibed with 76.8 wt% liquid electrolyte displays a power conversion efficiency of 9.5%, compared to 8.8% for the liquid electrolyte. This difference is primarily attributed to suppression of back electron transfer through the PGE. Hong et al. have induced in-situ gelation by UV radiation to discern the effectiveness of a BCP composed of poly(p-hydroxystyrene) and poly(ethylene oxide-co-propylene oxide) as a PGE. This design yields DSSCs possessing relatively high conversion efficiency along with improved long-term stability. A different approach combines a hole-transporting medium such as doped polypyrrole (PPy) with 1-butyl-2,3-dimethylimidazolium iodide (BDI) to produce a redox-coupling liquid. Addition of a poly(vinyl alcohol) copolymer subsequently converts the liquid into a PGE. The resultant DSSCs reveal efficiencies up to 4.7%. Similarly QS electrolytes consisting of SEOS BCPs afford efficiencies up to 6.7%, depending on the copolymer composition (which largely governs the nanoscale morphology that develops at equilibrium). Unexpectedly, the most favorable copolymer morphology for electrolyte diffusion appears to lack long-range order. In our previous studies, we have introduced a new thermoplastic elastomeric BCP archetype for use in photovoltaic devices. Even without the presence of a TiO$_2$ layer, sulfonated block ionomers (SBIs), multiblock copolymers possessing a charged midblock (illustrated in Scheme A.1), can be loaded with oppositely-charged, hydrophilic photosensitive dyes to yield nanostructured photovoltaic elastomer gels (PVEGs) that possess excellent mechanical properties even when hydrated. Their photon conversion efficiency is higher than that of similar hydrogel-based photovoltaic devices. The morphologies of these materials and, in turn, their photovoltaic performance can be independently controlled by solvent casting and solvent vapor annealing, as well as hydrothermal treatment (which can
yield a disordered ion-continuous morphology).\textsuperscript{55,56}

In this study, our objective is to establish the utility of SBIs as a PGE host for iodide/tri-iodide redox-couple liquid electrolytes in the fabrication of QS-DSSCs. Of particular interest here, we report that both hydrophilic and hydrophobic photosensitizers can be used in conjunction with these SBIs due to their solvent-tunable morphologies that can be designed to possess either continuous or discrete ionic microdomains.

**Experimental**

**Materials**

A series of three homologous poly[\textit{tert}-butylstyrene-\textit{b}-(ethylene-alt-propylene)-\textit{b}-(styrene-co-styrenesulfonate)-\textit{b}-(ethylene-alt-propylene)-\textit{b}-\textit{tert}-butylstyrene] (TS-EP-sS-EP-TS) penta-block ionomers with different ion exchange capacities (IECs) – 1.0, 1.5 and 2.0 – were kindly provided by Kraton Polymers (Houston, TX). For brevity, these materials are henceforth designated as SBlx, where \( x \) denotes the IEC value. According to the manufacturer, the number-average weights of the TS, EP and S blocks in the parent BCP were 15, 10 and 28 kDa, respectively (with an overall polydispersity ranging from 1.05 to 1.10). Fluorine-doped tin oxide-coated (FTO) glass with a sheet resistance of 8–10 \( \Omega \)/sq and an optical transmission of > 80% in the visible range was purchased from Nippon Sheet Glass (Tokyo, Japan). Anatase TiO\(_2\) colloids (Ti-Nanoxide D/SP, diameter \( \sim \)13 nm) and nanoporous TiO\(_2\) (Ti-Nanoxide R/SP, diameter \( \sim \)200 nm) were obtained from Solaronix (Aubonne, Switzerland). Platinum (Plastisol T/SP, Solaronix) constituted the counter electrode. Three ruthenium-based photosensitive dyes were examined during the course of this study: N719 (Ruthenizer 535-bisTBA from Solaronix), NCSU-10 and HD-15 (the latter two were synthesized and developed at North
Carolina State University, as described elsewhere. The chemical structures of these dyes are depicted in Scheme A.2. The commercial liquid electrolyte is HI-30 iodolyte (Solaronix). Reagent-grade toluene (T), isopropyl alcohol (IPA), tetrahydrofuran (THF), acetonitrile (A), tert-butyl alcohol (TBA), dimethyl sulfoxide (DMSO), and deoxycholic acid (DOA) were purchased from Sigma-Aldrich (St. Louis, MO) and used as-received.

**Methods**

Dye-sensitized solar cells were prepared by adapting a previously reported fabrication procedure. For each working electrode (photoanode), FTO glass was screen-printed with TiO$_2$ by doctor-blading. A double layer of TiO$_2$ was first produced using the anatase TiO$_2$ colloids deposited at a thickness of ~10 μm over a square area measuring 0.18 cm$^2$. Nanoporous TiO$_2$ was deposited as a thin layer (ca. 12-14 μm thick) by screen-printing and sintered at 500°C for 1 h under vacuum. The dye solutions were prepared at a constant concentration of 2 × 10$^{-5}$ M in a 1:1:1 w/w/w A/TBA/DMSO mixture, and DOA was added as a co-adsorbent at a concentration of 20 mM. The TiO$_2$-plated photoanode was immersed and held in each dye solution for 20 h at ambient temperature to adsorb the dye onto the TiO$_2$ surface. For the counter electrodes, FTO glass was first cleaned in an ultrasonic bath containing 10% HCl(aq) and acetone for 15 min. A layer of quasi-transparent Pt paste was screen-printed on the FTO glass and sintered at 450°C under vacuum. In-situ gelation of the electrolyte proceeded by the addition of 2 wt% SBI cast from either THF as a polar solvent or a 70/30 T/IPA mixture (abbreviated TIPA) as a nonpolar/polar solvent to commercial HI-30 iodolyte, which contains iodide/tri-iodide, ionic liquid, lithium salt, a pyridine derivative, and thiocyanate in acetonitrile. The TiO$_2$ photoanode with adsorbed dye and the Pt-counter electrode were
ultimately assembled with the PGE into a sandwich-type cell without any sealing adhesive (since the SBI inherently behaves as a pressure-sensitive adhesive), as illustrated in Figure A.1. Each assembly was wrapped in aluminum foil and stored in an oven maintained at 50°C (to prevent moisture absorption) until analyzed.

The photocurrent of each of the QS-DSSCs produced here was measured at ambient temperature in a solar simulator (WXS-155S-10) operated at AM 1.5 illumination (with a light intensity of 1000 W/m²). The solar simulator was calibrated using a standard ORIEL Si solar cell (Newport, Stratford, CT). Light illuminated the cell through the FTO glass from the anode side, and incident-photon-to-current conversion efficiency (IPCE) measurements were performed on a CEP-2000 system (Bunkoh-Keiki, Hachioji, Japan). Transmission electron microscopy (TEM) was conducted with a JEOL JEM-2200FS microscope (operated at 200 kV) on SBI specimens prepared by first staining the sulfonic acid groups in as-cast bulk films with Pb acetate and then embedding the stained films in epoxy prior to ultramicrotoming to obtain electron-transparent sections. Back-scattered scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDS) elemental data were acquired at 10 kV with an ultrahigh-resolution FEI Verios 460L microscope equipped with an Oxford X-ray detector to ascertain the morphological characteristics and composition gradients across the SBI/TiO₂ heterojunction. Specimens were cast between two Si wafers in the same deposition process as described above for the QS-DSSCs. The wafers were scored with a diamond knife, and the samples were subsequently cryofractured in liquid nitrogen. Elements unique to particular compounds of interest (e.g., Ti for TiO₂ nanoparticles) were used to identify the location of said compounds. Small-angle X-ray scattering (SAXS) was performed at the Advanced Photon
Results and Discussion

QS-DSSC Fabrication

The schematic diagram featured in Figure A.1 illustrates the sandwich-style architecture of the QS-DSSCs prepared in this study. In each specimen, one of the ruthenium dyes pictured in Scheme A.2 is adsorbed onto the sintered TiO₂ layer, whereas the ionic microdomains of the SBI are selectively imbibed with the iodide-based electrolyte. As observed from the TEM images of the SBI2.0 material included for comparison in Figure A.1, the SBI morphologies are largely dictated by the choice of casting solvent. When THF, a polar solvent, is used for this purpose, the as-cast morphology consists of alternating lamellae and dispersed cylinders (only lamellae are shown in Figure A.1 because they are expected to be representative of the equilibrium morphology). In this case, the ionic channels are contiguous, thereby expediting electron diffusion through the PGE. In marked contrast, films cast from the mixed TIPA co-solvent promotes the formation of dispersed ionic microdomains residing in a nonpolar matrix (due presumably to the presence of T, which possesses a higher normal boiling point, and therefore evaporates slower, than IPA). Although the ionic microdomains appear as discrete spheroidal micelles, we have previously reported⁵⁵,⁵⁶ that TIPA-cast SBI films possessing this morphology are capable of swelling, and this disordered morphology can transform into a bicontinuous network of polar and nonpolar microdomains, upon even short-time exposure to a polar solvent (such as water). It is therefore important from the TEM images
provided in Figure A.1 to bear in mind that the casting solvent is, for the most part, responsible for the initial contiguity of the electron-transferring, electrolyte-containing ionic microdomains. No solvent vapor annealing is performed here since it would tend to drive the morphology towards its equilibrium (lamellar) state.

The effect of added HI-20 iodolyte on the morphology of SBI2.0 is evident from the scattering profiles supplied in Figure A.2. In this figure (generated by azimuthal integration of 2D scattering patterns), scattered intensity is presented as a function of the scattering vector (q), where q = 4πsin(θ/2)/λ, λ is the wavelength of the X-ray radiation (0.087 nm) and θ is the scattered angle. Several important morphological metrics can be extracted from such profiles. For example, the microdomain spacing, calculated from the position of the principal scattering peak in the structure factor (at q*) according to Bragg's law (2π/q*), constitutes a measure of the average center-to-center microdomain distance. For TIPA-cast SBI2.0 films without iodolyte (dry), the mean spacing between ionic micelles is 34.7 nm. This value changes to 30.1 and 31.6 nm for SBI1.5 and SBI1.0, respectively. When SBI2.0 is cast from TIPA with iodolyte, the microdomain spacing increases to 39.7 nm, suggesting nanostructural swelling. As explained elsewhere, the profiles can be fit in the mid-q region (≈ 0.2-2.0 nm⁻¹) with a spherical form factor to approximate the micellar core radius: 15.0 nm for the dry TIPA-cast SBI2.0 and 20.2 nm for the iodolyte-imbibed analog. These estimates provide additional evidence of nanoscale swelling and suggest that the ionic domains expand by ≈150 vol%. Further, the features become less well defined (i.e., broader) upon incorporation of the iodolyte, suggesting a substantial increase in the size and shape dispersity. This change is similar to that which we have previously observed for SBI films swollen in water, which is
comforting given the polar nature of the iodolyte. In comparison, the spacing between ionic lamellae and cylinders (as deduced by structure factor peaks positioned at $2q^*$, $\sqrt{7}q^*$, and $\sqrt{12}q^*$) in dry THF-cast SBI2.0 films is 45.4 nm and reduces to 39.7 and 40.4 nm for SBI1.5 and SBI1.0, respectively. Once again, when SBI2.0 is cast in the presence of iodolyte (from THF), the domain spacing swells to 56.4 nm and the peak definition decreases. In fact, the remaining structure factor peaks discernible at only $q^*$ and $3q^*$ suggest that (i) the films are almost entirely composed of lamellae and (ii) the ionic and nonionic phases are nearly equal in thickness (supported by estimation of the lamellar thicknesses: 27.3 and 29.1 nm for the ionic/iodolyte-rich and nonionic phases, respectively). The ionic domains in this case are estimated to expand by 67 vol%. Although addition of iodolyte clearly swells and distorts the ionic microdomains in SBI films cast from either solvent, they do not compromise the microphase-separated nanostructure. Prior studies of PGEs report\textsuperscript{47} that the transition from an ordered BCP morphology to a less ordered, yet still microphase-separated, one has little effect on conductivity. We shall return to discuss this issue further in a later section.

Thus far, we have addressed the solvent templating of the SBI homologues employed in this study and their ability to swell, but remain microphase-ordered, in the presence of the liquid electrolyte intended to promote electron transfer. In this section, the results obtained from SEM and EDS are presented to interrogate the morphological and chemical features of the SBI/TiO$_2$ heterojunction. The orthogonally-arranged cross-sectional SEM images displayed in \textbf{Figure A.3a} indicate a relatively sharp delineation between the TiO$_2$ nanoparticles that form a porous packing layer without any noticeable evidence of absorbed SBI and the SBI-rich PGE containing a few dispersed TiO$_2$ particles. These images suggest the existence of an
interface measuring less than ~0.5 μm across. Included in Figure A.3a are averaged elemental traces generated along the interface normal from elemental maps collected by EDS. To avoid variations due to position along the interface, 2D elemental maps have been collapsed into 1D concentration gradients across the cross-section by summing X-ray counts at each point in ImageJ. Within each distinct region of the QS-DSSC, the elemental concentrations are relatively constant. In contrast to the sharp transition evident in the SEM images, however, the elemental transition across the SBI/TiO₂ interface appears more diffuse. The titanium trace (from TiO₂) reveals that the interface is broad, measuring ~1.8 μm across, whereas the interfacial thicknesses determined from the carbon and iodine traces (due to the SBI and redox reagent, respectively) are somewhat narrower at ca. 0.9 to 1.2 μm. These results demonstrate that a nontrivial concentration of TiO₂ has penetrated within the PGE, which is not surprising considering the loosely packed surface of the TiO₂ layer shown in Figure A.3b. This observation conversely reveals that the SBI-based PGE absorbs to a finite extent into the porous TiO₂ layer during the casting process when polymer solution flows into the TiO₂ pores. The volume of polymer solution deposited on the surface of the TiO₂ layer is, on average, 10 μL with little variation from one cell to another. Interestingly, the concentrations of iodine and carbon appear to be closely coupled, verifying the affinity of the iodolyte for the ionic regions in the SBI matrix. These regions are expected to provide pathways for rapid electron diffusion to and from the cathode during light harvesting, as discussed below.

QS-DSSC Performance

A series of QS-DSSC devices has been fabricated according to the illustration portrayed in Figure A.1 wherein N719 dye molecules have been adsorbed onto the surface of
the porous TiO$_2$ layer, and the SBI-based PGE contains 10 µL HI-30 iodolyte. In **Figure A.4**, the responses of the three different SBI homologues differing in midblock IEC are compared. The resulting photocurrent density-voltage ($J$-$V$) curves measured under conditions of standard air mass 1.5 global (AM 1.5 G) and an intensity of 1000 W/m$^2$ are provided in **Figure A.4a**, which immediately establishes that the QS-DSSCs composed of SBI2.0 exhibit the best light harvesting performance in the series. Conventional solar cell parameters extracted from these $J$-$V$ curves are listed in **Table A.1** and indicate that the open-circuit voltage ($V_{oc}$) and fill factor ($FF$) are relatively constant at 0.72-0.77 V and 0.56-0.60, respectively, in the IEC series. An increase in midblock IEC correspondingly promotes increases in the short-circuit photocurrent density ($J_{sc}$) and the solar energy conversion efficiency ($\eta$). While the QS-DSSCs composed of SBIs with the lowest IEC levels (1.0 and 1.5) possess similar $J_{sc}$ values (~7 mA/cm$^2$) and $\eta$ values (~3%), $J_{sc} = 15.14$ mA/cm$^2$ and $\eta = 7.0\%$ in the case of SBI2.0-containing cells. The observed reductions of $J_{sc}$ and $\eta$ with decreasing midblock IEC are accompanied by comparable trends in the IPCE measurements provided as a function of light wavelength in **Figure A.4b**. All three devices prepared with different SBI grades show a relative IPCE maximum between 300 and 400 nm in the UV-Vis region and qualitatively similar behavior beyond 700 nm. The QS-DSSC consisting of the SBI with the highest IEC exhibits the highest IPCE (> 65%) most likely due to the SBI morphology. At the low IEC levels, SBIs possess lamellae with discontinuous ionic pathways (as ascertained from dry, ion-stained sections examined by TEM) that adversely affect electron transport, yielding maximum IPCE values just over 40%. This is not the case for SBI2.0, which is why all further measurements will focus exclusively on QS-DSSCs containing only SBI2.0.
Another significant consideration in the design of nanostructured QS-DSSCs composed of hydrophilic and hydrophobic microdomains is the polarity of the dye employed, since this will dictate the spatial distribution of the dye within the PGE. The commercial hydrophilic N719 dye pictured in Scheme A.2 serves as the benchmark in this study, whereas the NCSU10 and HD15 dyes introduced by El-Shafei and co-workers\cite{57,58} are designed to (i) enhance light harvesting and $J_{sc}$ through the incorporation of ancillary carbazole ligands and (ii) explore the role of additional hydrophobicity (due to the long alkyl chains on HD15) on overall efficiency. In the presence of conventional liquid electrolytes that are necessarily polar, the alkyl chains on HD15 hinder dye regeneration and lower the overall efficiency, in which case NCSU10 affords the highest efficiency of the three dyes examined here. As alluded to earlier, the morphology of the SBIs can be solvent-templated so that the ionic regions exist as continuous lamellar channels or dispersed spheroidal micelles (cf. Figure A.1). In the case of PVEGs (non-DSSCs designed without electrolyte or TiO$_2$), we have previously demonstrated that the SBI morphology can have a pronounced impact on the performance of hydrogel photovoltaic devices containing two oppositely-charged hydrophilic dyes derived from 9,10-dimethoxy-2-anthracenesulfonic acid sodium salt [DAS$^-$ Na$^+$] and tris(2,2'-bipyridine)dichlororuthenium(II) hexahydate [(Ru(bpy)$_3$)$_2$$^{2+}$ (Cl$^-$)$_2$]. A critical difference between the PVEGs and QS-DSSCs is that, in the latter, contiguous ionic microdomains must provide a highly permeable pathway for redox reagents to diffuse after reduction at the Pt anode to regenerate the dye at the TiO$_2$ interface. By varying the SBI morphology through the use of different casting solvents, we can investigate the efficacy of the three dyes in PGEs varying in matrix polarity. With this objective in mind, Figures A.5a and A.5b display the $J$-$V$ curves
acquired for QS-DSSCs containing SBI2.0 cast from THF and TIPA, respectively, along with each of the dyes depicted in Scheme A.2. It is comforting to see that, in all cases in both figures, the measured responses are superior to those from the cells containing SBIs with lower IEC values, thereby suggesting that a critical IEC is necessary for sufficient electrolyte loading, morphological development and, ultimately, electron transport. Device metrics extracted from these curves are included for comparison in Table A.1.

In Figure A.5a, use of THF as the casting solvent ensures that the ionic microdomains within the SBI2.0-based PGE are continuous, according to TEM images such as those featured in Figure A.1. The relatively small-molecule hydrophilic dye N719 provides the highest $J_{sc}$ and $\eta$, as discussed earlier. Interestingly, the HD15 dye functions better than the NCSU10, which is opposite to their relative performance in a liquid electrolyte. This difference presumably reflects the THF-cast SBI2.0 morphology, which consists, for the most part, of alternating hydrophilic and hydrophobic lamellae. Corresponding values of $J_{sc}$ and $\eta$ achieved with HD15 are 12.45 mA/cm$^2$ and 5.2%, respectively. When the casting solvent is changed to TIPA so that the ionic microdomains appear to be dispersed spheroidal micelles embedded in a hydrophobic matrix, QS-DSSCs fabricated with the hydrophobic HD15 outperform cells produced with the other two dyes ($J_{sc} = 14.75$ mA/cm$^2$ and $\eta = 6.3\%$). Such improvement in photoconversion suggests that the continuous, hydrophobic matrix of SBI2.0 helps to distribute the bulky HD15 molecules along the TiO$_2$ interface so that dye regeneration is no longer the efficiency-limiting step. The role of the carbazole ligands cannot be underestimated, since the NCSU10 dye yields a higher $\eta$ than N719 (5.1% versus 4.1%) in the TIPA-cast cells. Corresponding IPCE values measured from the THF- and TIPA-cast PGEs in the presence of
the N719 (Figure A.6a) and HD15 (Figure A.6b) dyes are consistent with the $J-V$ curves supplied in Figure A.5. The hydrophilic N719 dye is more effective in THF-cast specimens due to the continuity of the ionic microdomains, whereas the HD15 dye yields superior results when the TIPA-cast morphology possesses a hydrophobic matrix. The HD15 dye also tends to exhibit higher IPCE values (with a maximum of 66.3% at 540 nm) than N719, especially in the UV-Vis region below 400 nm. The results presented in Figures A.5 and A.6 confirm that dye polarity can therefore be matched to the solvent-templated SBI morphology to achieve optimum performance in terms of both $J-V$ and IPCE measurements. This outcome is in general agreement with the findings of Leandri et al.,$^{60}$ who report that a hydrophilic dye performed better than a hydrophobic one in a water-based electrolyte due to greater interfacial contact between the photosensitized anode and the electrolyte.

**Conclusions**

Ongoing development of organic solar cells has yielded a variety of different designs that exploit the versatility of polymeric materials to realize moderate to high photoconversion efficiency at relatively low cost. In this spirit, we have fabricated DSSCs that implement a relatively new thermoplastic elastomer (TPE) archetype, which consists of glassy endblocks, rubbery midblocks and a styrenesulfonate core, as the host for a liquid electrolyte. Unlike conventional TPEs that are completely nonpolar and typically exhibit moderate to strong thermodynamic interblock incompatibility (which drives self-assembly), the SBI homologues introduced here are amphiphilic and significantly more incompatible due to the presence of ionic species along the charged block. We have previously established that these materials, without the integration of a TiO$_2$ layer, yield dye-sensitized PVEGs that outperform other
hydrogel-like photovoltaics and retain robust mechanical properties even when hydrated. In this study, we introduce these SBIs into the fabrication of QS-DSSCs. Incorporation of the SBIs enhances both performance and design tunability by (1) penetrating into the TiO₂ layer and thereby improving electron transfer from the electrolyte to the photosensitized dye molecules, (2) serving as an intrinsic adhesive for the cells without requiring other sealing materials, and (3) permitting the use of either hydrophilic or hydrophobic photosensitizers due to the unique characteristic of the SBIs to be solvent-templated. Small-angle scattering data confirms that the SBI morphology largely remains intact, but the ionic microdomains swell, upon addition of the liquid electrolyte, which confirms electron transport along a continuous pathway. As expected, the photocurrent density and, hence, conversion efficiency depend on the extent to which the SBI is sulfonated due to both morphological and conductivity considerations. Because the morphologies of the SBI materials can be solvent-templated to yield either alternating lamellae or disordered ionic channels within a hydrophobic matrix, photosensitizers differing significantly in hydrophilicity can be used to achieve moderately high efficiencies (6.5-7.0%) without fabrication optimization. The QS-DSSCs investigated here provide evidence that the use of midblock-charged, network-forming block copolymers that behave as mechanically-tough and recyclable TPEs affords a highly desirable combination of properties for future solar harvesting endeavors.

Acknowledgments

H. A. A.-M. is grateful for a doctoral fellowship from the Ministry of Higher Education of Saudi Arabia. K. P. M. acknowledges the NC State Nonwovens Institute,
MANN+HUMMEL GmbH and the U.S. Department of Energy, and D. P. A. thanks Becton-Dickinson Technologies and Eastman Chemicals, for financial support. We are indebted to Dr. B. Lee (Argonne National Laboratory) for assistance with the SAXS data acquisition and Dr. G. N. Parsons (NC State University) for the use of his solar simulator. The authors acknowledge use of the NC State Analytical Instrumentation Facility, which is supported by the State of North Carolina and the National Science Foundation. This research used resources of the Advanced Photon Source, a U. S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

References


Table A.1. Solar cell characteristics extracted for SBI-based QS-DSSC devices from the $J$-$V$ curves reported in this study.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Casting solvent</th>
<th>Dye</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>SBI1.0</td>
<td>THF</td>
<td>N719</td>
<td>6.57</td>
<td>0.73</td>
<td>0.56</td>
<td>2.7</td>
</tr>
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<td>SBI1.5</td>
<td>THF</td>
<td>N719</td>
<td>7.37</td>
<td>0.72</td>
<td>0.60</td>
<td>3.2</td>
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<tr>
<td>SBI2.0</td>
<td>THF</td>
<td>N719</td>
<td>15.14</td>
<td>0.77</td>
<td>0.59</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>HD15</td>
<td>12.45</td>
<td>0.70</td>
<td>0.59</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>NCSU10</td>
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<td>0.73</td>
<td>0.54</td>
<td>4.2</td>
</tr>
<tr>
<td>TIPA</td>
<td>N719</td>
<td></td>
<td>10.34</td>
<td>0.72</td>
<td>0.54</td>
<td>4.1</td>
</tr>
<tr>
<td>TIPA</td>
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<td></td>
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<td>0.73</td>
<td>0.57</td>
<td>6.3</td>
</tr>
<tr>
<td>TIPA</td>
<td>NCSU10</td>
<td></td>
<td>10.48</td>
<td>0.71</td>
<td>0.67</td>
<td>5.1</td>
</tr>
</tbody>
</table>
Scheme A.1. Chemical structure of the sulfonated block ionomer (SBI) used to form polymer gel electrolytes in QS-DSSCs in this study.

Scheme A.2. Chemical structures of the three photosensitizer dyes employed in this study (labeled): HD15 (hydrophobic), NCSU10 (hydrophilic) and N719 (hydrophilic).
Figure A.1. Schematic illustration of the QS-DSSC fabricated with a sulfonated block ionomer (SBI) as the polymer gel electrolyte. The TEM images in (a) and (b) display the SBI2.0 morphologies (with the ionic regions selectively stained to appear dark) generated by solvent casting from THF and TIPA, respectively.
Figure A.2. SAXS profiles acquired at ambient temperature from TIPA-cast (black) and THF-cast (green) SBI2.0 before (dry) and after incorporation of the HI-30 iodolyte (labeled). The filled arrowheads identify the principal scattering peak, \( q^* \), in each profile, whereas the open arrowheads mark higher order scattering peaks (ratios to \( q^* \) labeled).
Figure A.3. In (a), cryofractured cross-sectional SEM image of a QS-DSSC containing the THF-cast SBI2.0 imbibed with HI-30 iodolyte. The averaged elemental traces for titanium, carbon and iodine track the spatial distribution of TiO$_2$, SBI and iodolyte, respectively, across the SBI/TiO$_2$ heterojunction. While the dashed blue lines on the SEM images identify the apparent interface, the solid/dashed lines indicate a broader interface on the basis of elemental composition. The SEM image in (b) displays the diffuse surface of the TiO$_2$ layer prior to SBI deposition.
Figure A.4. Photocurrent density presented as a function of voltage under the conditions specified in the text (a) and incident photon conversion efficiency (IPCE) shown as a function of wavelength (b) for QS-DSSCs containing THF-cast SBI grades differing in midblock IEC: 1.0 (△), 1.5 (●) and 2.0 (○). The solid lines serve to connect the data.
Figure A.5. Voltage dependence of the photocurrent density for QS-DSSCs containing (a) THF- and (b) TIPA-cast SBI2.0 with the three different photosensitizers depicted in Scheme A.1: NCSU10 (△), HD15 (●) and N719 (○). The solid lines serve to connect the data.
Figure A.6. Wavelength dependence of the IPCE for QS-DSSCs containing THF- (○) and TIPA-cast (●) SBI2.0 with the photosensitizers (a) N719 and (b) HD15. The solid lines serve to connect the data.