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SYNTHESIS AND CHARACTERIZATION OF CHEMICALLY FUNCTIONALIZED SHAPE MEMORY NANOFOAMS FOR UNATTENDED SENSING APPLICATIONS

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SYNTHESIS AND CHARACTERIZATION OF CHEMICALLY FUNCTIONALIZED SHAPE MEMORY NANOFOAMS FOR UNATTENDED SENSING APPLICATIONS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Material Science
& Engineering

by
Anna Paola Soliani
December 2014

Accepted by:
Dr. Igor Luzinov, Committee Chair
Dr. Marian Kennedy
Dr. Olin Mefford
Dr. Marek Urban
ABSTRACT

The work in this dissertation is devoted to the synthesis and characterization of novel materials for off-line unattended sensing: shape-memory grafted nanofoams. The fabrication process and characterization of highly efficient, polymeric nanosensor element with the ability to selectively detect analytes and retain memory of specific exposure events is reported. These shape memory nanofoams could potentially act as efficient and highly sensitive coatings for evanescent waveguide-based optical monitoring systems. On exposure to specific analytes, the polymeric coatings locally change their internal structure irreversibly at the nanolevel, affecting the local optical properties such as refractive index.

Currently, enrichment polymer layers (EPLs) are currently being used to detect of chemical vapors. EPLs are thin polymer films that can increase signal of an analyte through absorption. These films are designed to interact with analytes via chemical interactions while this analyte is present in the environment. Once the analyte is removed from the environment surrounding the EPL, these EPLs have no residual memory of the interaction(s). This dissertation will address this limitation in the field of chemical unattended sensing through the use of functionalized polymeric films that possess ability to retain memory of analyte exposure. Specifically, we will use chemically cross-linked gradient nanofoam as a material with built-in analyte-specific sensing properties.

A novel method has been created to fabricate chemically functionalized shape memory nanofoams. First, a polymer film containing epoxy groups is deposited onto a
substrate. Then, the film is cross-linked via reaction of the epoxy groups to create a non-soluble, yet swellable coating. This film is then treated with specific chemical substances capable of reacting with the epoxy functionalities. This procedure is necessary to convert the epoxy groups into various functional moieties. This process generates a chemically modified orthogonal gradient film whose composition is unique at each point across the surface of the film. Lastly, shape memory properties are imparted to the film by swelling it in a solvent with high affinity (“good”) with the polymers and freeze-drying it under reduced pressure.

Using this methodology, a shape memory nanofoam gradient film was produced that could “remember” its original non-porous shape. This “memory” occurs through the following process. Exposure of the foamed film to an analyte causes local plasticization of the film, making the polymer thickness decrease (“shrink”). Since the film possesses graded chemical composition, locations of the film interact in different ways to each analyte. Specifically, only certain regions in the film (which have specific thermodynamic affinity to the chemical) shrink, creating a unique thickness pattern targeted for each chemical. The resulting changes in local film morphology are irreversible and provide a permanent record or “fingerprint” for the chemical event of interest. Ultimately, the films can be prepared on the surface of waveguide arrays to allow optical monitoring at different locations, for unattended sensing purposes.

In conclusion, this dissertation provides the fundamental knowledge for synthesis of orthogonal chemical gradient nanofoam films. The methods are reported as a novel way of producing responsive polymer nanofoams for unattended sensing purposes. The
results complement and add to the current state of the art materials used in the field of
unattended sensing.
DEDICATION

I dedicate my dissertation to my family. My loving parents, Mario and Daniela Soliani, had a continuous desire to see me improve, become successful, and provided never-ending support. My brother, Giulio, also showed patience, kindness, and provided me with strength throughout the years.

Finally, I would like to dedicate this work to both Ryan McBath and my closest friends, in appreciation of their words of encouragement, help, and compassion.

Everything that I am currently and will ever be is a product of what these friends and family have given me.
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I would like to show appreciation to the faculty of the department, for being outstanding mentors that assisted me with this project. Their excitement and willingness to provide feedback made this research an enjoyable experience. Specifically, I would like to acknowledge Dr. Gary Lickfield and Dr. Deborah Lickfield for their immense support, dedication, and feedback during each of my accomplishments and set-backs.

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1 INTRODUCTION

1.1 Introduction

This dissertation is devoted to the synthesis and characterization of novel materials for off-line unattended sensing: shape-memory grafted nanofoams. The major goal is to create a highly efficient, nanoscale, polymeric sensor element that can selectively detect analytes and retain memory of specific exposure events. It is expected that these shape memory nanofoams can act as efficient and highly sensitive coatings for diverse evanescent waveguide-based optical monitoring systems. On exposure to specific analytes, the polymeric coatings locally change their internal structure irreversibly at the nanolevel, which affects local optical properties such as refractive index and optical absorption.

Enrichment polymer layers, (EPLs), have been already used for detection of chemical vapors.\(^1\) EPLs are defined as thin polymer films (≤5 µm) deposited onto a sensor surface that can increase signal or facilitate detection of an analyte through absorption. The films interact with the analytes via chemical or physical interactions, which cause a temporary deformation in shape, for example, by swelling. Once the analyte is removed from the environment, traditional EPLs have no residual knowledge of the interaction.\(^2\)\(^-\)\(^4\)

To this end, this dissertation has the purpose to address limitations of the current EPLs in the field of chemical unattended sensing via the use of functionalized polymeric films that possess ability to retain memory of the analyte exposure. Specifically, the
current research uses chemically cross-linked gradient nanofoam as a material with built-in analyte-specific sensing properties. The synthesis of the film is achieved in four major steps as shown in Figure 1.1.

![Figure 1.1](image)

**Figure 1.1.** Synthesis steps to produce a chemically cross-linked gradient nanofoam as a material with built-in analyte-specific sensing properties.

First, a polymer film containing epoxy groups in monomeric units is deposited on a substrate. Then, this film is cross-linked via reaction of the epoxy groups to create a non-soluble, but swellable coating. The extent of the cross-linking is controlled so that only a fraction of the epoxy groups are consumed by the reaction. Next, the film is treated with different substances capable of reacting with the epoxy functionality. This procedure is necessary to convert the epoxy groups into various functional moieties. This generates a chemical orthogonal gradient film whose chemical composition will be unique at each
point across the surface of the film. Lastly, shape memory properties are imparted to the film by swelling it in a good solvent and freeze-drying it under reduced pressure.

Using this methodology, a shape memory nanofoam gradient film is produced. More specifically, the coating (which is not in thermodynamic equilibrium in the porous state) is able to “remember” its original non-porous shape determined by the network elasticity. Exposure of the film to an analyte that interacts with the functionalities of the film causes local plasticization of the film by lowering the $T_g$ of the polymer chains and the film locally shrinks. In fact, since the film possesses graded chemical composition, different locations of the film interact in a different way with the target chemical. Specifically, only certain regions in the film (which have specific thermodynamic affinity to the chemical) shrink, creating a unique thickness pattern targeted to a specific chemical (Figure 1.2).

![Figure 1.2](image)

**Figure 1.2.** Schematic representation of the expected components and nanofoam behavior. Exposure to different analytes yield selective and specific response: A specific and selective response for one chemical functionality, B specific and selective response for a different chemical functionality, and C for both functionalities (complete selectivity).

The resulting changes in local film morphology are irreversible and provide a permanent record or “fingerprint” for the chemical event of interest. The only way to erase the pattern is via exposure of the film to the same good solvent that is the original environment to allow the chains to collapse and return to their original shape. Ultimately,
the films can be prepared on the surface of waveguide arrays to allow optical monitoring at different locations, for unattended sensing purpose.

In this dissertation, Chapter 2 gives a thorough background of current state of the art in fields related to this work, such as enrichment polymer layers and shape memory polymers, in the effort to determine the current gaps in detection mechanisms and unattended sensing. Specifically, Chapter 2 reveals that there are numerous polymers that have been shown to have macro level response to external stimuli and that are currently used as sensors. The extensive literature also shows that limited to no work, to the best of our knowledge, has been done to achieve a successful novel nanomaterial that can detect multiple analytes and retain long-lasting memory of specific exposure events.

Chapter 3 lists and describes the materials used in this work. In addition, it provides a detailed explanation of the analytical techniques used, as well as what equipment was utilized to characterize the polymer films.

Chapter 4 is dedicated to the fabrication of shape memory polymer nanofoams using two different polymers. These two polymer layers differ by the extent of epoxy groups in the chain. This was done to understand the limitations of the foaming technique as well as to understand the mechanism and the extent of foaming that is achievable for both systems. It is found that the polymer having fewer epoxy groups, foams to a larger extent. The nanofoams displayed shape memory characteristics as they went back to their original shape (morphology and thickness) when exposed to the original environment. Atomic Force Microscopy (AFM) is shown to be a powerful tool, capable of monitoring the change in morphology. In addition, nanotomography experiments revealed that the
nanofoams have a porous structure that is present throughout the entire layer. Chapter 4 also shows that the anchoring layer has an imparted selectivity to different analytes. The change in refractive index upon foaming and collapsing was calculated and shows that the change is significant enough to be monitored via change in thickness.

Chapter 5 focuses on the fabrication and functionalization of the shape memory polymer nanofoams using a number of chemical substances. The chemical functionalization was achieved using carboxy-terminated polystyrene (PS-COOH) and ethanol amine (EA). The substances are shown to penetrate the film structure allowing for chemical modification within the entire layer. Upon the functionalization, the nanofoams retain shape memory properties. It also shown that, where the specific functionality is present, each analyte acts as a plasticizer, causing a localized response (partial collapse). As in Chapter 4, the change in refractive index (RI) as a function of change in thickness was monitored. Finally, in Chapter 5, it is shown that the optical micro-disk resonators can serve as a feasible platform for employment of chemically functionalized shape memory nanfoams for unattended sensing.

Chapter 6 discusses gradient chemical functionalization of nanofoams. The synthesis and characterization of a 1D one and two-component nanofoam films are reported. Ellipsometry and AFM revealed that, anywhere along the sample, the chemical composition ratio between layer components is unique. The unique chemical composition is what drives the detection mechanism, as it makes each location have a selective and specific response to the analytes. In addition, due to the different level of grafting at each unique composition, it is possible to produce a nanofoam with a featureless surface across
the entire geometry of the sample. As reported for **Chapter 4** and **Chapter 5**, the change in morphology was straightforwardly monitored with AFM. The response mechanism to the various analytes indicates that the extent of the foam collapse at different places of the gradient is determined by the thermodynamic quality of the solvent. Consequently, it was found that each geometrical position showed unique fingerprint for each solvent type.

Statistical analysis performed on the results presented in **Chapter 6** revealed that, within 95% confidence, there is a significant difference in the variance between the most analytes used. Finally, **Chapter 6** concludes that a successful 1D one and two-component system gradient shape memory nanofoam films were produced, with significant specificity and selectivity. In addition, the extent of response reveals that it is possible to detect and identify the analyte as a function of chemical composition.

**Chapter 7** takes the results of **Chapter 6** and adds one key component that ultimately improves the detection mechanism: the formation of orthogonally placed chemical gradients. 2D one and two-component systems are discussed. All systems were synthesized step by step to reveal the possibility for formation of an orthogonal chemical gradient shape memory nanofoam. The orthogonality not only adds chemical functionalizations (added selectivity to the system), but also adds specificity as each point across the orthogonal gradient has a 3-component unique composition. Ellipsometry and AFM confirm that the uniquely localized chemical composition drives the detection mechanism and improves on the 1D chemical gradients. As in **Chapter 6**, not only each location has a selective and specific response to the analytes, but a nanofoam with a
featureless surface across the entire geometry of the sample is produced. With the orthogonal chemical gradients, a unique fingerprint for each solvent type is recorded. Again, statistical analysis performed on the results presented in Chapter 7 revealed that, within 95% confidence, there is a significant difference in the variance between the analytes used.

Finally, Chapter 7 concludes that a 2D one- and two-component orthogonal gradient shape memory nanofoam material was produced, with further improved specificity and selectivity than the results in Chapter 6. More importantly, it is shown that these newly developed orthogonal chemically modified shape memory nanofoams are efficient elements to be used for unattended sensing purposes.

In conclusion, this dissertation provides the fundamental knowledge for synthesis of orthogonal chemical gradient nanofoam films. The methods are reported as a novel way of producing responsive polymer nanofoams for unattended sensing purposes. The results complement and add to the current state of the art materials used in the field of unattended sensing.

1.2 References


2 LITERATURE REVIEW

2.1 Introduction

Investigation in the field of enrichment polymer layers (EPLs) deposited on waveguides has generally focused on determining one specific polymer to target efficiently one specific analyte. Although the EPLs developed to this date are deemed efficient at recognizing one specific analyte, they are far from being utilized for “universal sensors”. This chapter aims to review the key aspects of EPL synthesis, including the identification of polymers for selectivity, which have been studied and researched in the last few decades. Various characterization methods as well as quantitative analysis of targeted analytes will be discussed. Chapter 2 aims to prove fundamental basis of the areas that are important for enrichment polymer layers used as sensors, as well as show the limitations of current research and technology.

2.2 Sensing with Polymer Layer

2.2.1 Sensing of chemical vapor targets with polymer thin-film

The development of simple, safe, and non-intrusive sensing equipment used to selectively detect specific chemicals has been of great priority. A chemical sensor furnishes information about its environment and consists of a physical transducer and a chemically selective layer. A biosensor contains a biological entity such as enzyme, antibody, bacteria, and tissue as recognition agent, whereas a chemical sensor does not contain these agents.
Effective approaches to sensors have traditionally made use of “lock-and-key” designs (Figure 2.1). Specifically, a receptor is synthesized in order to be highly selective and interact with the target analyte. In addition, extensive work has been done in modeling using computational design of receptor and sensor proteins with novel functions. Another approach uses a physiochemical effect toward a single chemical. As much as such approaches are appropriate for the detection of a single analyte, they require the synthesis of a separate selective sensor for each target compound to be detected.

![Figure 2.1. General Schematic of a chemical sensor with lock and key design, where a receptor is synthesized in order to be highly selective and interact with the target analyte.](image)

A lot of techniques used to impart recognition (or selectivity) to sensors are based on interactions between the substrate and biological molecules. Such interactions have been proven to be unstable. Significant work done in sensing with polymers deals with molecularly imprinted polymers (MIPs). MIPs are defined as polymers that are typically generated via the interaction of monomers with one functionality and a target element, usually using a cross-linking agent. In such systems each functionality is only specific to a target molecule. For these sensing devices to work efficiently, it is required to have a flexible polymer to facilitate a fast equilibrium between releasing and up taking of
target molecule, whilst being rigid enough to maintain integrity. In addition, the polymers need good thermal and mechanical stability. ⁶,⁷

The important step towards multiple detections was in 1996 when Lonergan et al. described a responsive sensor array based on carbon black composites and demonstrated that this array was able to detect various vapors and vapor mixtures. ⁸ The individual sensor elements were constructed from films consisting of carbon black particles dispersed into organic polymers. The carbon black imparts electrical conductivity to the films and the different organic polymers produced the chemical diversity between elements in the sensor array. Swelling of the polymer upon exposure to a vapor increased the resistance of the film, thereby providing monitoring in the presence of a vapor. Since a different polymer composition was present on each sensor element, an array of elements responded to a wide variety of vapors (or complex mixtures of vapors) in a distinctive, identifiable fashion (Figure 2. 2). ⁸

Figure 2. 3 shows the resistance change of two carbon black–polymer composite films during repeated, periodic exposures to a test solvent vapor. The resistances of the films increased when the solvent vapor was present and then returned to their original baseline values after the vapor flow was discontinued. In addition, the resistance was unique for each system. This was one of the first successful multi-array sensors produced. ⁸
Figure 2. Schematic of a chemiresistor sensor array and the response profiles generated by such an array. In this work, an array of 17 conducting carbon black–polymer composites has been used. The resistance of each composite is monitored and observed to increase upon swelling by organic vapors. The open arrow in the schematic is a time marker corresponding to the introduction of solvent vapor and the solid arrow to its removal. The maximum relative differential resistance changes (ΔRmax/R) for the elements of the array during exposure to the test vapor provide a fingerprint that can be used to classify various analytes. Reprinted (adapted) with permission from 8. Copyright 2014 American Chemical Society.
Figure 2.3. Resistances, $R$, of carbon black composites of (a) PEVA and (b) PVP upon 15 repeated exposures to benzene (at 1.1 ppt) and methanol (at 1.5 ppt), respectively. The PEVA composite was fabricated from a 15% (w/w) carbon black mixture and the PVP composite from a 45% (w/w) carbon black mixture. Both composite films were deposited onto glass slides. The exposure periods were for 15 s during which time the resistances increased as shown. These exposures were interlaced between recovery periods in which the resistances decreased. These traces demonstrate the good reproducibility and stability that can be achieved with carbon black composites. Reprinted (adapted) with permission from 8. Copyright 2014 American Chemical Society.
Another detection mechanism that has been investigated is systems with enrichment polymer layers. EPLs can be defined as thin polymer films (≤5μm) deposited onto a sensor surface that can increase signal or facilitate detection of an analyte through absorption. Examples of EPLs include incorporating fluorescent dyes whose fluorescence decrease when exposed to analytes or other indicators that can be monitored. The films interact with the analytes via chemical interactions, which cause the system to deform, for example, by swelling. Once the analyte is removed the layers de-swell, and no residual knowledge of the interaction with the type of analyte is available.

2.2.2 Responsive Polymers

EPLs can be considered as responsive polymer systems since they react to different stimuli via chemical interactions. This feature is used for targeting analytes for sensing applications. To this end in the past few decades, considerable interest has been placed on polymer systems that are responsive to external stimuli. These systems can effectively and irreversibly alter their structure and response depending on the type of stimuli. Currently, all environmental triggers can be classified in three major components: chemical, biological, and physical. The “response” of a polymer can be defined in various ways. Responsive polymers in solution are typically classified as those that can change their individual chain dimensions/size, secondary structure, and/or their solubility. Generally, the chemical or physical events which cause these responses are limited to, for example, forming or destroying secondary forces (electrostatic or hydrophobic interactions) or to the simple reactions of moieties in the polymer backbone. In other systems, the definition of a response can be expanded to include more dramatic
alterations in the polymeric structure, such as either reversible or irreversible bond breakage of the polymer backbone or cross-linking groups.\textsuperscript{13}

### 2.2.2.1 Biologically Responsive Polymers

The number of reported works in biologically responsive polymer systems involves glucose-responsive polymers based on the GOx-catalyzed reaction of glucose with oxygen. Typically, glucose-sensitivity is caused by the response of the polymer to the byproducts (specifically, gluconic acid and H\textsubscript{2}O\textsubscript{2}) that result from the oxidation of glucose (Figure 2.4).\textsuperscript{15}

![Figure 2.4](image)

**Figure 2.4.** (a) In the absence of glucose, the PAA chains are extended which lowers the permeability of the membrane. (b) Addition of glucose leads to a lowering of local pH and chain collapse due to a reduction in electrostatic repulsion. \textsuperscript{15} Reprinted with permission from Elsevier, Copyright 2014.
Therefore, incorporating a polymer that responds to either of these molecules can lead to a glucose-responsive system. Peppas et al. did extensive research in this field by preparing glucose-responsive hydrogels. Poly(methacrylic acid (PMAA)-graft-ethylene glycol) gels were synthesized in the presence of GOx. At neutral and high pH values, the gels swelled due to the repulsion between the negative charges present on methacrylate units. The reduction in pH upon oxidation of glucose consequently leads to collapsing of the gel. Hydrogels prepared by copolymerization of N-isopropylacrylamide (NIPAM) with methacrylic acid have also been reported.

2.2.2.2 Redox/Thiol Sensitive Polymers

Redox/thiol sensitive polymers are another class of responsive polymers used specifically for controlled drug delivery. The interconversion of thiols and disulfides is a key step in many biological processes. Because disulfide bonds can be reversibly converted to thiols by exposure to various reducing agents and/or undergo disulfide exchange in the presence of other thiols, polymers containing disulfide linkages can be considered both redox and thiol-responsive (Figure 2.5).
Stayton and co-workers produced a drug carrier by copolymerization of a pyridyl disulfide containing acryloyl monomer with methacrylic acid and butyl acrylate. [9] The resulting terpolymers were both thiol- and pH-sensitive and can disrupt the membrane, which is necessary for effective gene delivery. Tsarevsky and Matyjaszewski synthesized redox/thiol-sensitive polymers using a disulfide-functional dimethacrylate monomer (Figure 2. 6) to synthesize redox sensitive nanogels via inverse miniemulsion ATRP. [10]
2.2.2.3 Electro-responsive Polymers

Electro-responsive polymers can be used to prepare materials that bend, swell, and/or shrink in response to an electric field. Electro-responsive polymers can transform electrical energy into mechanical energy and consequently have applications in artificial muscle actuation, sensing, and controlled drug delivery. Kim et al. prepared a semi interpenetrating polymer network (IPN) hydrogel of PHEMA and chitosan. The response of the hydrogel to an applied electric field was investigated through measurements of bending rate and angle, with these values increasing with ionic strength of the medium and applied voltage. Most polymers that exhibit electro-sensitive behavior are polyelectrolytes, although a few neutral polymers can also be employed if an additional charged or polarizable component is present. Zrinyi and co-workers synthesized a lightly cross-linked poly(dimethyl siloxane) gel containing electrosensitive colloidal TiO$_2$ particles (Figure 2.7) which displayed rapid bending of the gel in silicon oil.

Figure 2.7. Electro-response of a PDMS gel loaded with 10% TiO2 as a function of uniform field strength. Reprinted with permission from Elsevier, Copyright 2014.
2.2.2.4 Photo-responsive Polymers

Photo-responsive polymers change their properties when irradiated with light of the appropriate wavelength. Typically these changes are the result of light-induced structural transformations of specific functional groups along the polymer backbone or side chains. Applications of photoresponsive polymers include polymer viscosity control, photomechanical actuation, bioactivity, and drug delivery. Wang et al. presented photo-induced deformation of epoxy-based azobenzene-containing polymer colloids. Depending on the wavelength of irradiation, these photo-responsive colloids were able to change their morphology from spheres to spindles and eventually to rods. Ghadiri et al. produced a new photo-responsive peptide system composed of two ringshaped cyclic peptides bound by an azobenzene moiety. When the azobenzene group is in the trans state, the cyclic peptide units experienced intermolecular hydrogen bonding, yielding extended linear chains. On the other hand, UV-induced isomerization to the cis state led to intramolecular hydrogen bonding and, consequently, depolymerization of the supramolecular complex (Figure 2.8).
Figure 2.8. Photo-responsive supramolecular assembly/disassembly of cyclic peptides tethered by azobenzene units, as reported by Ghadiri and co-workers. Reprinted (adapted) with permission from 8,25. Copyright 2014 American Chemical Society.
Extensive work has been achieved in the field of sensitive polymers. Specifically, a lot of literature in respect to identifying different types of mechanism of response has been reviewed. These systems can effectively and irreversibly change their structure. Such mechanisms of response can be used for targeted and efficient sensor applications.

2.3 Shape memory polymers

Another field that is of interest for sensor applications is shape memory polymers (SMPs). Related to responsive polymers, SMPs respond to an external stimulus, but have the added effect of remembering the stimuli post-exposure. Consequently, such materials can be used as responsive materials for unattended sensing purposes.

2.3.1 Materials with shape memory characteristics

As discussed in Section 2.2.2, responsive materials have drawn considerable interest due to their great scientific and technological significance. Recently, a lot of work has been done with Shape Memory Materials (SMMs), specifically with Shape Memory Polymers (SMPs) and Shape Change Materials (SCMs). Such materials react to environmental changes in a pre-determined matter and to a predictable extent. It is important to distinguish between SMPs and SCMs. If the shape change is spontaneous and instant in the presence of the right stimulus, this is an SCM. Examples of SCMs are elastic rubber, piezoelectric materials, and liquid crystal. Shape change polymers (SCPs) and SMPs both have a basic molecular architecture that is a polymer network, but the mechanisms underlying the active movement are different. Both polymer concepts are based on functional components or stimuli-sensitive domains as switches. A SCM
changes their shape gradually, e.g. shrinkage as long as a suitable stimulus is applied, but they recover their original shape as the stimulus is terminated. In contrast, SMPs will only recover their original shape when the same external stimulus that induced the shape change is applied.  

Fundamentally from energy point of view, the difference between SCMs and SMPs is due to the storage capability of energy. The change in internal energy of materials accounts for the shape change in SMPs. In other words, shape memory is a process that enables the reversible storage and recovery of mechanical energy through a cyclical change in shape. In contrary to SMPs, in SCMs during the deformation process the external energy is transferred into a change in entropy.  

For a material to be classified as having a shape memory effect, it has to follow a simple mathematical model:

\[ R_f = 1 - \frac{E_r}{E_g} \]  
\[ R_t = 1 - \frac{f_{ir}}{\left[ \left( 1 - \frac{E}{E_g} \right) \frac{f_x}{f_{ir}} \right]} \]

where \( E_g \) is the glassy modulus, \( E_r \) is the rubbery modulus, \( f_{ir} \) is the viscous flow strain and \( f_x \) is the strain when the time is greater than the relaxation time. A high elasticity ratio \( (E_g/E_r) \) allows for a great resistance to the deformation at temperatures before the deformation temperature. It has been established that the polymer material has to be designed to meet the above criteria for shape memory applications.
In a SMP there are at least two segments (or domains): an elastic component and a transition component, which is able to alter its stiffness in the presence of a specific stimulus (Figure 2.9). External stimuli can include heat, electricity, light, and chemical. To date, researchers have used materials with these pre-determined shape memory functions and used them in various applications, such as biomedical, sensing, and actuators.

Figure 2.9. Molecular mechanism of the thermally induced shape-memory effect $T_{\text{trans}}$ = thermal transition temperature related to the switching phase. Reprinted with permission from Elsevier. 29

2.3.1.1 Thermally Responsive SMPs

The most widely used class of shape memory materials is thermal-responsive SMPs. The shape memory phenomenon in SMPs is a result of two structural features, one determining the permanent shape and the other having a thermal transition within a certain temperature range. Each of the shapes is determined by the elasticity of the polymer network. SMPs can be “frozen” in a temporary, thermodynamically unstable form by means of material immobilization via vitrification (transition into glass) or crystallization. Consequently, upon exposure to environmental stimuli, the material is
capable of returning to its original, thermodynamically stable state due to the elastic energy stored in the SMP network. An important group of physically cross-linked thermo-responsive shape-memory polymers are linear block copolymers, which include polyurethanes and polyetheresters. In polyesterurethanes, the urethane segments act as hard segments, while poly(ε-caprolactone) forms the switching segment Figure 2.

Another class of thermoplastic shape-memory polymers with $T_{\text{trans}} = T_{\text{g}}$ are polyesters. In co-polyesters based on poly(ε-caprolactone) and poly(butylene terephthalate), the poly(butylene terephthalate) segments act as the physical cross-linkers.

Kumpfer et al. developed multi-responsive SMPs by using covalently cross-linked metallosupramolecular polymers. Low molecular weight poly(butadiene) was end-capped with 4-oxy-2,6-bis(N-methylbenzimidazolyl)pyridine(-OMebip) ligands that with the addition of metal salts formed high molecular weight metallo-supramolecular
polymers. The addition of a tetra-functional thiol along with a photo-initiator results in mechanically stable films. These films consist of a soft poly(butadiene) phase and a hard metal ligand phase (Figure 2.11).
Kumpfer et al. deformed the films at 100°C. That shape was maintained until the
sample was reheated to that same initial temperature (Figure 2.12).  

Figure 2.12. Standard thermal one-way shape-memory cycle for a film of Eu(NTf$_2$)$_3$. The film is deformed at 100°C
 to a set force, and the temperature is reduced while the force is held constant. The force is removed, and the strain
fixing is determined. Heating the sample back to 100°C followed by cooling to room temperature allows the material to
recover its original shape. Reprinted (adapted) with permission from 42. Copyright 2014 American Chemical Society.

Sun et al. in 2010 discuss at length the thermo-responsive properties of an ester-based thermoplastic polyurethane SMP prepared from diphenylmethane-4,4’-diisocyanate, adipic acid, ethylene glycol, ethylene oxide, polypropylene oxide, 1,4-butanediol and bisphenol A. 37 It is reported that a piece of such SMP is able to fully recover to its original shape upon heating after a severe quasi-plastic deformation (up to 400% tensile strain). 37, 43 In 2012, Wang et al. reported results of a hybrid SMP which has both the cooling(thermo)-responsive shape memory effect and water-responsive SME. 44 The hybrid is comprised of a plastic sponge, acting as the elastic component, filled with Poloxamer 407 (P407) gel, the transition component. It was observed that the hybrid was able to recover its original shape within a minute when immersed into 0 °C
water. In contrast, when immersed into 20 °C water, the recovery time was one hour (Figure 2. 13). \(^{44}\) The higher speed shape recovery is due to the melting of P407 gel at 0°C, while slower speed shape recovery is due to the dissolution of P407 gel in 20 °C water (which is well above the cooling melting temperature range of P407 gel. \(^{44}\)

Thermal-responsive SMPs are widely used in biomedical applications because numerous polymers are known to have a transition temperature around that of human body-temperature (37°C). Consequently, such materials are easily loaded with drugs and frozen in a dormant shape at room temperature (i.e. below their transition temperature) and when the loaded polymer reaches the blood stream, it will relax to its original structure and release the drug. \(^{36, 45}\) Recently, Langer et al. synthesized a biodegradable shape memory polymer made of photoset oligo(e-caprolactone) dimethacrylates and butyl acrylate (BA) as comonomer. \(^{46}\) In these materials, the shape transition temperature \(T_{\text{trans}}\) is conditioned by the melting of crystallizable oligo(e-caprolactone) segments, approximately 43°C and 49°C. \(^{46}\) In addition, large bulky devices can be introduced into the body in a compressed temporary shape by means of minimally invasive surgery and then be expanded on demand to their permanent shape. This is achieved via a physical response or a thermal response. \(^{31, 47-49}\)

Metzger et al. in 2002 present an SMP microactuator for treating ischemic stroke. The SMP microactuators were made from two different ester-based thermoset polyurethanes (Composition proprietary of Hayashi and Fujimura, 1991). \(^{50}\)
Figure 2.13. (a) Cooling-responsive SMP in hybrid. (cooling response), (b) Shape recovery in 0 °C water , c) Shape recovery in 20 °C water. Reprinted with permission from Elsevier.
Each was supplied with a two part liquid system which consisted of a resin and a hardner. The shape was fixed at 80°C in either a film shape, or as a coil, using a brass mold with a coil shaped cavity (Figure 2.14).  

![Figure 2.14. SMP microactuators in straight (a) and coiled (b) shapes after shape change at 80°C. Reprinted with permission from Springer.](image)

The results for clot removal feasibility were determined by the maximum force and pressure against which the microactuator coil can hold a clot (which should be larger than those expected in physiological systems). Two main conclusions were assessed. The first is that the device can hold the clot against pressures greater than those found in neuro-vascular systems. The second was that, as seen in Figure 2.15, there is sharp drop off in maximum pressure as the vessel size increases, implying there is a correlation between vessel diameter and microactuator SMP diameter.
In 2007, Baer et al. investigated the thermomechanical properties of a series of Mitsubishi SMPs for potential application as medical devices. The SMPs used were obtained from DiAPLEX Company (similar to Metzger et al. [50]) either as two part thermoset resins or thermoplastic resin in pellet form. The compositions are proprietary, but it is known that the material is segmented polyurethane, which has a microphase separated morphology. Baer et al. measured the glass transition temperatures and moduli by differential scanning calorimetry. Tensile tests were performed with 20 and 100% maximum strains, at 37°C and 80°C, which are body temperature and actuation temperature, respectively (Figure 2. 16). At a given temperature test, the materials exhibited very similar curves, with quite different strains at break. The maximum strain at break was 100% at 37°C and 270% at 80°C. These polyurethanes appear particularly well suited for medical applications in deployment devices such as stents or clot extractors.
2.3.1.2 Thermally activated SMPs via Molecular Interactions

One other reported method to trigger the SMP shape change other than thermal activation is using molecular interactions between the triggering molecule and the SMP. For example, such interactions would include disruption of hydrogen bonding in the SMP network since the molecules act as plasticizers. Plasticizing the structure reduces its glass transition temperature. Yang et al. and Lv et al. used chemical inputs (water and dimethyformamide respectively) to trigger the shape change in the SMPs.\textsuperscript{37,52}

Stimuli-responsive hydrogels that undergo abrupt changes in volume in response to external stimuli such as solvent composition have potential applications in biomedicine. Miyata et al. report a material which swells reversibly in a buffer solution in response to a specific antigen.\textsuperscript{53} The hydrogel was prepared by grafting the antigen and corresponding antibody to the polymer network, so that binding between the two introduces cross-links.
in the network. Competitive binding of the free antigen triggers a change in gel volume owing to breaking of these non-covalent cross-links (Figure 2.17).  

![Diagram of a suggested mechanism for the swelling of an antigen–antibody semi-IPN hydrogel in response to a free antigen. Reprinted with permission from Nature Publishing group.](image)

- : Antibody-immobilized polymer chain
- : Antigen-immobilized polymer chain
- : Free antigen

**Figure 2.17.** Diagram of a suggested mechanism for the swelling of an antigen–antibody semi-IPN hydrogel in response to a free antigen. Reprinted with permission from Nature Publishing group.

As seen in Figure 2.18, the antigen-responsive swelling was examined upon reaching equilibrium. The water content of the equilibrated hydrogels was calculated to be 97 wt%. The swelling ratio of the antigen–antibody semi-IPN hydrogel increased abruptly following the addition of free rabbit IgG antigen.  

Furthermore, the swelling ratio of the polyacrylamide semi-IPN hydrogel was independent of the antigen concentration in the buffer solution, but the swelling ratio of the antigen–antibody semi-IPN hydrogel was strongly dependent upon it. This indicates that the latter hydrogel has an antigen-sensing function.  

No work was reported to show responses to chemical vapor analytes.
Figure 2.18. The equilibrium swelling ratio of the PAAm semi-IPN hydrogel (open circles) and the antigen–antibody semi-IPN hydrogel (filled circles) in phosphate buffer solution at 25 °C as a function of antigen concentration in the buffer solution. The swelling ratio of the hydrogels was determined by the ratio of their changing diameters, which were measured in the solution using an optical microscope. Reprinted with permission from Nature Publishing group.

2.3.2 Sensing with SMPs

The unidirectionality of the thermal transition in SMPs is advantageous in sensing applications, as it makes tampering with the SMPs sensor elements difficult or even impossible. Other applications for shape memory materials include sensors and actuators. In 2000, Abraham Lee released one of the first patents in microfabricated therapeutic actuators from shape memory materials, formed using a poly-urethane base polymer. Since, a lot of progress has been accomplished. Currently, known systems include one-way and two-way actuators. Examples of one way system include segmented thermoplastic polyurethanes (TPUs), which consist of an amorphous soft segment and a crystalline hard segment. Their shape memory effect utilizes the amorphous soft segment domain as reversible phase and the crystalline hard segment.
An example of a two way actuator system is the work by Ahir et al. in 2006. They fabricated new thermoplastic liquid-crystalline elastomers using tri-block co-polymers, taking advantage of the subsequent phase separation and plasticization that occur above the nematic–isotropic transition. It is labeled as two-way actuating, because it works in both directions of the transition.

2.3.3 Chemically modified SMPs

To date, a significant number of polymers have been designed and synthesized to demonstrate shape-memory properties for diverse applications, such as actuators, sensors, and biomedical devices. Chemo-responsive materials have a number of advantages and their potential applications are expected to be large. Their complex types of mechanisms challenge material design, guided largely by chemo-responsive materials of actuation. The complex molecular mechanism and design principles of chemo-responsive materials, as well as the nature of their responses, is incompletely understood and modelled, and much of the possible responses are not even mapped.

To the best of our knowledge, most work has been published on micro and macro scale objects that show shape memory properties. Limited work has been reported on doing such with nanoscale films. Further, there has been only limited study of methods for producing highly selective and engineered responses of SMPs to environmental stimuli. The bulk of the work to date has been directed towards generalized responses to stimuli which do not permit effective targeting and control of the features of SMPs.
2.4 Chemical Modification of surfaces

To be able to chemically modify surfaces, it is important to understand the different and most commonly used ways to do so. Extensive work in the past decades has been done to develop convenient and effective ways to modify polymeric surfaces. Chemical modification can be used on the surface of the sensors to heighten the response to specific analytes.

2.4.1 Grafting methods

Grafting of polymers is currently a widely used method for modifying and functionalizing solid surfaces, including stimuli responsive ones. End-functionalized polymer chains may be grafted to the solid substrate (grafting to) or the grafting reaction can proceed by polymerization from the surface (grafting from). The processes of polymer functionalization and grafting are becoming increasingly important in advanced materials technology, particularly in applications when it is necessary to impart some specific property to the polymer, such as biomedical, electronics, and sensing.

“Grafting to” is often used for the surface modification of materials which already have excellent bulk properties. Implied is that this can be performed if the substrate surface has suitable functional groups. The “grafting to” technique involves reaction of functionalized polymer chains with the (complementary) functional groups of the surface, resulting in the formation of tethered chains. One of the major advantages of the “grafting to” method is that the polymer used can be characterized, functionalized and treated in various ways before reacting it with the surface of the substrate. In addition,
different molecular weight and polydispersity polymers can be used, although polymers with a narrow molecular weight distribution produce better defined brushes.

While the end use of the biofunctionalized polymer varies with each application, the overall concept is the same, as illustrated in Figure 2.19.

Figure 2.19. Examples of polymer systems comprising polymer brushes. Reprinted with permission from Elsevier.
The first step is to select a polymer with bulk properties needed for the ultimate application. Since most commercial polymers are not functionalized, surface functionalization is needed for the attachment of a bioactive compound(s), which can be achieved via grafting. Kingshot et. al, grafted poly(ethylenimine) to a surface onto which PEG was already attached, which results in a high PEG density resulting, ultimately, in reduced protein adhesion. Kang et. al synthesized fluoropolymer surfaces with new and specific functionalities, such as metal-free conductivity, biocompatibility, and bondability to metals just by choice of functional monomers for graft copolymerization. Stamm et. al discussed at length the synthesis of adaptive and switchable surfaces and thin polymer films both fabricated from two incompatible carboxyl-terminated polymers chemically grafted to silicon substrates. These two grafted polymers form the mixed (binary) brushlike layer. They provided a thorough theoretical analysis of the phase segregation that occurs in these in binary brushes using the “grafting-to” method. Specifically, they showed how complicated phase diagrams and film morphologies can be produced. Zhao et. al provide an extensive review of different polymer systems comprising of polymer brushes. The work of Auroy et al. showed the linear relationship of polymer brush heights with respect to the degree of polymerization of the tethered polymer chains. To achieve such, they chemically end-grafted polydimethylsiloxane (PDMS) chains on porous silica particles and performed neutron scattering.

Currently, “grafting to” brushes are predominately used in sensing applications, for example as enzyme logic gate sensors. The majority of sensor devices utilize many
polymers with definite roles, either in the sensing mechanism or through immobilizing the species responsible for sensing of the analyte component. Piletsky et al. presented a new technique for coating microtitre plates with molecularly imprinted polymers (MIPs), specific for low-molecular weight analytes such as epinephrine, atrazine and proteins. They polymerized 3-aminophenylboronic acid (APBA) (Figure 2. 20a), 3-thiopheneboronic acid (TBA) (Figure 2. 20b), and aniline in water by oxidative polymerization, and grafted the polymers onto the polystyrene surface of the microplates.

![3-aminophenylboronic acid and 3-thiopheneboronic acid](image)

**Figure 2. 20.** 3-aminophenylboronic acid (APBA) (a), 3-thiopheneboronic acid (TBA). Reprinted with permission from Elsivier.

Dupont-Filliard et al. described the design of a new versatile and reversible DNA sensor in which they immobilized single strands of DNA to provide advantages such as high sensitivity and versatility of use. Their design was based on biotin grafting-units which were covalently linked to a polypyrrole matrix. The grafting units were also regenerated after the denaturation of the biotin linkage, which then allows a new biomolecule to be immobilized with the possibility to generate a new sensor. In addition, Livache et al. produced an oligonucleotide (ODN) array constructed on a silicon device with 50-micron microelectrodes. Each electrode was covered by a conducting polymer (polypyrrole) grafted with ODN. Finally, Marcel et al. prepared a receptor
layer by the molecularly imprinted photo-polymerization of acrylamidomethylpropanesulfonic acid and methylenediacrylamide. They grafted the polymer layer onto a gold electrode surface which was coated with an alkanethiol monolayer. These results were the first reversible chemosensor for creatinine based on artificial chemoreceptors reported.\textsuperscript{78}

The “grafting to” method has some drawbacks. The major one is that this method is considered a “self-limiting” process. In other words, the polymers chains have to diffuse through the forming polymer layer to be able to reach the reactive sites on the surface of the substrate. This phenomenon progresses as the thickness of the grafted polymer layer increases.\textsuperscript{79}

The “grafting from” technique involves polymerization that is initiated at the substrate surface by attached (usually covalently bonded) initiating groups (Figure 2. 21).

\textbf{Figure 2. 21.} “Grafting from” SIP consists of attaching a covalently bound initiator functionalized adlayer to a surface and performing an \textit{in situ} polymerization. Reproduced from Ref.\textsuperscript{74} with permission from The Royal Society of Chemistry.
Reactions commonly used to achieve this are conventional radical polymerization, reversible addition fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP). Generally, the initiators are immobilized onto the surface followed by in situ surface initiated polymerization to generate the tethered polymers. Most of the time, the immobilization of the initiators requires multiple steps, which may lead to low graft densities of initiators. In addition, another drawback is that it is challenging to control how much initiator is immobilized.

“Grafting from” is also used for biomedical applications. More specifically, extensive research has been conducted on irradiation induced grafting. For instance, Ratner et al. graft polymerized 2-hydroxyethyl methacrylate (HEMA), ethyleneglycol dimethacrylate (EGDMA), and N-vinyl pyrrolidone (NVP) onto the surface of silicone films. This was achieved by irradiating silicone in the presence of monomers with a Co source. Hari et. al grafted acrylonitrile (AN), HEMA, and acrylamide by swelling the samples in monomer solutions, followed by exposure the γ-irradiation. Grafting was done to silicone/urethane materials. For drug delivery purposes, Gref et al. grafted polysaccharides with polyesters to synthesize novel amphiphilic copolymers. Specifically, the synthesis of poly(ε-caprolactone) monocarboxylic acid (R−PCL−CO2H) was carried out by ring-opening uncatalyzed polymerization of monomer in the presence of a carboxylic acid. R−PCL−CO2H was then reacted with carbonyl diimidazole, and the resulting imidazolide was further reacted with dextran to obtain amphiphilic copolymers (Figure 2.22).
“Grafting from” does not seem to be widely used for chemical sensing as much as it is for biosensing. In addition, most of the work consisted in using this grafting technique to synthesize polymer brushes to just enhance currently existing sensors. Most state of the art is focused on thiol-based self-assembly techniques, which work well with noble metals and can, in most cases, generate supramolecular architectures which can be functionalized for potential biosensing applications. Supramolecular architectures of biomolecules based on silane coupling chemistries on silicon dioxide substrates are commonly used in many applications. Kambhampati et al. used the “grafting from” technique to deposit PMMA brushes and synthesize stable silicon dioxide films on noble metals using a novel sol–gel technique. The films were...
functionalized with various reactive groups for biosensor applications. Colloidal particles have potential applications sensors, and polymer brushes can be used to stabilize them. For example, Deleuze et al. prepared P(nBA) polymer brushes from SiO$_2$ nanoparticles using nitroxide-mediated polymerization. The direct application would be for a chromatic sensor and separator. Other groups such as Morinaga et al. have used PMMA brushes prepared using ATRP for the same application.

The “grafting from” technique also has its drawbacks. Most of the time, the immobilization of the initiators requires multiple steps, which may lead to low graft densities of initiators. In addition, another drawback is that it is challenging to control how much initiator is immobilized.

2.4.2 Chemical Gradients for Sensing

Surface chemical gradients have attracted considerable attention for applications in biomolecular interactions, chemical affinity, nanotribology, and microfluidics. Different techniques to create gradients on various substrates have been proposed, which include templates, lithography, and temperature differences. Limited work has been identified about using more than one gradient as a sensing mechanism for multiple chemicals. In addition, the chemical gradients proposed are generally on the surface of the substrate/material, and not within a system.

2.5 Conclusion

In conclusion, a review of the literature showed that, to date, extensive work has been done in the areas of chemical modification of polymer films. Specifically, EPLs
have been studied as ways to efficiently target environmental stimuli for sensing applications. Recently, shape memory polymers have also shown to respond to various stimuli in a pre-determined way. The review also showed that there is no effective way of producing a universal sensor that is specific and selective to multiple environments and is able to retain memory of the exposure events.

To this end, the literature review of Chapter 2 revealed that there is no practical way of producing “universal sensors” capable of detecting multiple environments and being able to recognize (remember) the stimuli. New and efficient methods for unique and targeted chemical modification need to be developed.

2.6 References


44. Wang, C., Huang, W., Ding, Z., Zhao, Y., Purnawali, H., Cooling-/water-responsive shape memory hybrids. *Composites Science and Technology* **72** (10), 1178-1182.


3 MATERIALS AND METHODS

3.1 Chemical Reagents Used

3.1.1: Hydrogen peroxide:
Company Identification: AcrosOrganics.

MSDS Name: Hydrogen Peroxide (30% in Water) (Without Stabilizer), Reagent ACS.
Catalog Numbers: AC411880000, AC411881000, AC411885000.

3.1.2: Sulfuric acid 98%:
Company Identification: AcrosOrganics.

MSDS Name: Sulfuric acid, reagent ACS.
Catalog Numbers: 13361-0000, 13361-0010, 13361-0025.

3.1.3: Toluene:
Company Identification: AcrosOrganics.

MSDS Name: Toluene, reagent ACS.
Catalog Numbers: 424500-0000, 42455-0010, 42455-0250, 42455-5000.

3.1.4: Chloroform:
Company Identification: Acros Organic

MSDS Name: Chloroform ACS reagent
Catalog Numbers: 423550040.

3.1.5: Methanol:
Company Identification: Sigma-Aldrich

MSDS Name: Methanol Chromasolv for HPLC
Catalog Numbers: 34860-4XL-R

3.1.6: 2’,2’-Azobisisobutyronitrile, 98% (AIBN):
Company Identification: Sigma-Aldrich
MSDS Name: 2,2’-Azobis(2-methylpropionitrile)
Catalog Numbers: 441090

3.1.7: Acetone:
Company Identification: Sigma-Aldrich
MSDS Name: Acetone
Catalog Numbers: 34860-4XL-R

3.1.8: Glycidyl Methacrylate (GMA):
Company Identification: Aldrich
MSDS Name: Glycidyl Methacrylate
MSDS Name: Catalog Numbers: 151238

3.1.9 Methyl Methacrylate (MMA):
Company Identification: Aldrich
MSDS Name: Glycidyl Methacrylate
Catalog Numbers: 151238

3.1.10: Diethyl Ether:
Company Identification: Aldrich
MSDS Name: Glycidyl Methacrylate
MSDS Name: Catalog Numbers: 151238

3.1.11: Methyl ethyl ketone:
3.2 Structure of Polymers Used for Chemical Modification

3.2.1 Poly(glycidyl methacrylate) (PGMA) (Figure 3.1)

Figure 3.1. Structure of PGMA.

PGMA (M_n = 176,000 g/mol, M_w = 285,600 g/mol, PDI = 3.4, determined by GPC using polystyrene standards) was synthesized by solution free radical polymerization and purified by multiple precipitations in diethyl ether. The polymerization was carried out in MEK at 60 °C. AIBN was used as an initiator. The polymer obtained was purified by multiple precipitations from MEK solution in diethyl ether.¹
3.2.2 Carboxy Terminated Poly(styrene) (PS-COOH) (Figure 3. 2)

![Structure of carboxy-terminated Polystyrene](image)

**Figure 3. 2. Structure of carboxy-terminated Polystyrene**

PS-COOH was purchased from PolymerSource Inc. (M<sub>n</sub>=2,400 g/mol, M<sub>n</sub>=2,000 g/mol, PDI=1.2)

3.2.3 Hydroxy Terminated Poly(2-vinylpyridine) (PVP-OH) (Figure 3. 3)

![Structure of hydroxyl-terminated poly(2-vinylpyridine)](image)

**Figure 3. 3. Structure of hydroxyl-terminated poly(2-vinylpyridine).**

PVP-OH was purchased from PolymerSource Inc. (M<sub>n</sub>=5,700 g/mol, PDI=1.)
3.2.4 Ethanol Amine (EA) Structure (Figure 3. 4)

![Ethanol Amine Structure](image)

Figure 3. 4. Structure of ethanol amine (EA)

Ethanol amine (EA) was purchased from Sigma-Aldrich.

3.2.5 PMMA-co-PGMA random copolymer (Figure 3. 5)

![PMMA-co-PGMA Structure](image)

Figure 3. 5. Structure of PMMA-co-PGMA random 70:30 (x:y) copolymer.

Poly(methyl)methacrylate-co-poly(glycidyl)methacrylate (Mₚ=136,000 g/mol, PDI=2.7, determined by GPC using polystyrene standards) was synthesized free radically using 2,2’-azobisisobutyronitrile (AIBN) as initiator. Polymerization was conducted in a two-necked flask, equipped with a reflux condenser, nitrogen inlet and outlet, and a
magnetic stir-bar. 8.39 ml of methyl methacrylate (1.5M) and 4.49 ml of glycidyl methacrylate (0.45M) were dissolved in MEK and bubbled under nitrogen for 1 hour to remove residual oxygen in a Schlenk tube. 0.123g of AIBN (0.01M) was charged into the flask to initiate polymerization. Polymerization was conducted under a blanket of nitrogen for three hours at 45°C. The reaction was halted by placing the reaction vessel into an ice bath. The random copolymer obtained was purified by multiple precipitations from MEK solution into diethyl ether.

3.3 Principal Experimental Techniques

3.3.1 Cleaning Substrate

3.3.1.1 Silicon wafers

Highly polished single-crystal silicon wafers of [100] orientation were purchased from Broker and are used as a substrate. The wafers are first cleaned in DI water in an ultrasonic bath for 30 min, replacing the MilliQ water every ten minutes. They were then placed in a hot piranha solution (3:1 98% concentrated sulfuric acid and 30% hydrogen peroxide; the mixture reacts violently with organic solvents and should be handled with care) for 1 h, and then rinsed several times with MilliQ water.

3.3.1.2 Waveguide resonators

Vivek Singh, under the advisory of Anu Agarwal and Lionel Kimerling at MIT, fabricated and tested the microdisk resonators. The resonator samples were fabricated using UV photolithography with a negative lift-off photoresist. Four inch silicon wafers with 3 µm of thermal oxide were spin-coated with NR9-1000PY negative resist and
exposed through a chrome photomask with waveguide and resonator patterns. The chalcogenide glass (Ge$_{23}$Sb$_7$S$_{70}$) was deposited via thermal evaporation under vacuum ($\sim$3×10$^{-7}$ Torr) followed by resist lift-off in acetone and isopropanol. The resonators are carefully cleaned in acetone to remove any dust. They are not sonicated so as to maintain the waveguides and surface features intact.

3.3.2 Deposition of polymers via dip coating

Dip-coating technique was used for the preparation of the thin and thick polymer films on the substrates. With this method, the substrate is immersed into the polymer solution and withdrawn at a constant speed. The uniformity and thickness of the deposited film depend on this speed. In addition, any vibration of the substrate while in solution could alter the uniformity as well. All polymer samples were dip-coated using a Mayer Fientechnik D-3400 dip-coater in a clean room to avoid contamination of the clean substrates with dust particles. In order to generate films of different thicknesses, substrates were dip-coated into solutions of different concentrations.

3.3.3 Atomic Force Microscopy (AFM)

AFM was utilized to image the morphologies of the polymer films. Morphological imaging was done on a Dimension™ 3100 (Digital Instruments, Inc.) microscope in tapping mode in ambient air. Silicon tips from Micromasch. The tips utilized were silicon with a force constant of 40-45 N/m and a natural frequency of 160-168 Hz. All imaging, unless otherwise noted, was achieved with a scan rate of 1 Hz. All images resolutions are 256x256 pixels. Nanoscope III 5.12r3 was used for image processing.
3.3.4 Ellipsometry

3.3.4.1 Dry State Measurements

In general, ellipsometry measures the change in polarization of light reflected off the sample surface. Measurements in the dry state for all grafted substrates were carried out using a COMPEL automatic ellipsometer (InOmTech, Inc) at an angle of incidence of 70°.

3.3.4.2 In-Situ Ellipsometry

Swelling and collapse of the polymer nanofoams were measured using a closed cell containing a small beaker (approximately 1 ml in volume) filled with different solvents for 40 minutes, to allow time for the solvent to evaporate and reach saturation.

3.3.5 Reflectometry

Reflectometry was used to determine the change in thickness of the polymer after every dip coating and after exposure to each analyte at a wavelength of $651\lambda$. Spectroscopic reflectometry uses multiple wavelengths (colors) of light to obtain an array of data for analysis of film thickness and other film parameters.

3.3.6 Characterization of the Polymer Brush Films

Ellipsometric thickness of all components at particular point on the sample was used to calculate anchored chain density (chains/nm$^2$) of each component as described below. The surface coverage (attached amount), $\Gamma$ (mg/m$^2$), was calculated from the ellipsometric thickness of the layer, $h$ (nm) by the following equation:

$$\Gamma = h \rho$$  \hspace{1cm} \text{Eq. 3.1}
where $\rho$ is density of attached (macro)molecules. The density of PGMA (1.08 g/cm$^3$) was assumed to be the same as for poly(propyl methacrylate). The density data for PS (1.05 g/cm$^3$) and PMMA (1.17 g/cm$^3$) was available from supplier.

The anchored chain density ($\Sigma$, chains/nm$^2$), i.e., the inverse of the average area per adsorbed chain was determined by:

$$\Sigma = \Gamma / N_A * 10^{-21} / M_n = (6.023 * \Gamma * 100) / M_n$$  \hspace{1cm} \text{Eq. 3.2}

where $N_A$ is the Avogadro’s number and $M_n$ (g/mol) is the molar mass of the grafted polymer.

3.4 Thermal Stage

3.4.1 1D one- and two-component gradient stage

A copper stage of dimensions 1 cm in width by 3 cm in length was used to fabricate 1D one- and two-component gradient systems. Lengthwise, one side was heated to 175°C using a cartridge heater (Omega, Inc.). The opposite side was maintained to temperature using a circulating water bath held at 85°C. This produced a gradient from 175°C to 85°C.

3.4.2 2D one- and two-component gradient stage

A secondary stage was built with the intent to improve the heat transfer of the stage used to fabricate 1D one- and two-component gradients, as well as accommodate larger sample size (1 inch x 1 inch). Heat can be defined as a form of energy transfer from a high temperature location to a low temperature location. The three main methods of heat transfer are conduction, convection, and radiation. The rate of heat
transfer is key in the design and production of an efficient gradient thermal stage. The first variable that affects the rate of conductive heat transfer is the temperature difference between the two locations. The second variable is the materials involved in the transfer. The effect of a material is often expressed in terms of its thermal conductivity.\textsuperscript{3, 4} Higher thermal conductivity values imply that the material can transfer heat faster. The rate of heat transfer is directly proportional to the surface area through which the heat is being conducted. Finally, it is important to consider the distance that the heat must be conducted through.

The rate of heat transfer can be calculated using Equation 3.3 below.

\[
\text{Rate} = kA\left(\frac{T_1 - T_2}{d}\right)
\]

\text{Eq. 3.3}

where \(k\) is the thermal conductivity constant, \(A\) is the area, \(T_1\) and \(T_2\) are the two temperatures separated by \(d\), the distance.\textsuperscript{4}

The design of the stage included aluminum as the conductive metal and Teflon as an insulating agent. Four holes were placed equi-distant from each other (every one inch) with the function of heating or being heat sinks. The entire diameter of the stage was 3x1.5 inches. Thermocouple holes were also placed equidistant from each other and made so they measure the temperature every quarter of an inch at the middle of the sample. Figure 3. 6 shows the SolidWorks schematic of the stage (a) and the final product in (b).

In the designed aluminum stage, the heat transfer rate was calculated as 21.33 kW for one inch, knowing that the \(k_{Al}\) value for aluminum is 237 W°C /m. If copper had been used as a material (\(k_{Cu} = 398\) W°C /m), the heat transfer rate would have been 35.82 kW.
Figure 3.6. SolidWorks schematic of the stage (a) and the actual final aluminum thermal stage design (b)
3.5 References


4 SYNTHESIS AND CHARACTERIZATION OF SHAPE MEMORY NANOFOAMS

4.1 Introduction

Significant work was conducted in sensing using enrichment polymer layers (EPLs). EPLs can be defined as thin polymer films (≤5μm) deposited onto a sensor surface that can increase signal or facilitate detection of an analyte through its absorption into EPL. 1, 2 The films interact with the analytes via chemical or physical interactions, which cause the EPL to respond, for example, by swelling. Once the analyte is removed from the EPL, though, the layers de-swell, and typically no residual knowledge of the interaction with the type of analyte is available. 3-5 In the latter case, consequently, there is no memory of the response to the analyte. However, retaining memory of specific environmental exposure events is beneficial in the field of unattended sensing as it allows to have an “off-line” sensor that will record in real time the exposure and retain that information. To use EPLs for unattended sensing then, a different response mechanism than the one currently utilized is needed.

To create EPLs with permanent record of an exposure, shape memory materials (SMPs) can be employed. 6 Such systems have the ability to memorize a permanent shape and be manipulated to assume other temporary shapes. SMPs can be fixed in a temporary, dormant shape under specific conditions of temperature, stress, and environment. Later they can relax into the original, stress-free condition by imposition of a specific thermal, electrical, or environmental command. 6 Consequently, typical applications for shape
memory materials include sensors and actuators.\textsuperscript{7-10} However, SMPs can be used as prospective EPLs, having a permanent record of the exposures to the environment.

The most widely used class of shape memory materials is thermal-responsive SMPs. The shape memory phenomenon in SMPs is a result of two structural features, one having a thermal transition within a certain temperature range and the other determining the permanent shape. Each of the shapes is pre-determined by the elasticity of the polymer network.\textsuperscript{6, 11, 12} SMPs can be “frozen” in a temporary, thermodynamically unstable form via vitrification (transition into glass) or crystallization. When the vitrified system is exposed to an environmental stimuli, such as increase in temperature, the material is capable of returning to its original, thermodynamically stable state due to the elastic energy stored in the network. This thermal transition is uni-directional. This aspect could be advantageous for chemical sensing applications, as it would make tampering with the SMPs sensor network difficult or even impossible.\textsuperscript{6}

One other reported method to trigger a shape change other than thermal activation is by using molecular interactions between a triggering molecule and the SMP. The triggering molecule would be small enough to act as a plasticizer and reduce the glass transition temperature. A possible example of such an interaction is the disruption of H-bonding in an SMP network in the presence of an analyte, i.e. water.\textsuperscript{12,13}

To date, a significant number of polymers have been designed and synthesized to demonstrate shape-memory properties sensing applications.\textsuperscript{14} Most work has been published on micro and macro scale objects that show shape memory properties.\textsuperscript{6,11,12} To the best of our knowledge, no work has been reported on doing such with EPLs.
Furthermore, there has been only limited study of methods for producing highly selective and engineered responses of SMPs to environmental stimuli, as most systems take advantage of the inherent properties of the materials. [13] Using SMPs as nano-scale EPLs would allow highly selective and specific recognition of analytes with the added feature of a permanent recording of the environmental changes, which would satisfy all requirements for unattended sensing. Finally, solvent sublimation techniques have been used in the past for production of membranes, but never as a way to impart shape memory properties to a nanoscale film.

To this end, the primary focus of Chapter 4 is the fabrication and characterization of shape memory nanofoams as prospective EPLs with recording capabilities. To the best of our knowledge, fabrication of this type of shape memory polymer on the nanoscale has not yet been reported in the scientific literature. Additionally, using this new method of imparting shape memory properties, it is possible to accurately tailor the thickness of the resulting nanofoams.

Specifically, a base polymer layer that is swellable yet not soluble was produced. For this purpose, it was advantageous to use PGMA and PMMA-co-PGMA due to the epoxy groups available in their backbone structure. The base layers were successfully foamed and showed typical characteristics of shape memory materials as they collapse when re-introduced to their original environment. Films of two different thicknesses were investigated. The concentration of epoxy groups and their role in the ability to foam was also studied and revealed that the copolymer could foam to a larger extent than the more
cross-linked PGMA films. In addition, it was possible to accurately tailor the properties of the films, both for thickness and morphology.

4.2 Experimental

4.2.1 Grafting of base layers

4.2.1.1 Poly(glycidyl)methacrylate (PGMA)

Grafting of PGMA layers was achieved using the following procedure: first, the surface of a Si wafer was coated using a dip coating technique with a film of PGMA from either a 1% or 2% solution from chloroform to obtain films of different thicknesses. Next, the films were annealed in a vacuum oven at 120°C and 150°C for either 4 or 24 hours. The films were subsequently rinsed in chloroform three times for thirty minutes with solvent replacement every time.

4.2.1.2 Poly(methyl) methacrylate-co-poly(glycidyl)methacrylate (PMMA-co-PGMA)

The surface of the clean Si wafer were coated using a dip coating technique with a film of PMMA-co-PGMA from either a 1% or 2% solution in chloroform to obtain films of different thicknesses. Next, they were annealed at 150°C for 24 hours. The films were consequently rinsed in chloroform three times for thirty minutes with solvent replacement every time.

4.2.2 Foaming of base layers

Foaming is achieved in the same manner for all experiments presented. A chamber containing a copper stage that is cooled down to -85±5°C using a Dewar filled with liquid nitrogen. The temperature is maintained using a thermocouple Love Controls
32A. Once the low temperature is reached, the samples are covered with 500µL of chloroform, enough to swell the polymer film (Figure 4.1a).

Since swelling of the polymers is virtually instantaneous, as soon as the samples are exposed to liquid chloroform they are immediately placed on the cooled stage and frozen in their swollen state. Vacuum is then applied to sublimate the chloroform at a pressure of 50mTorr using an oil-free pump Edwards 6iC. Vacuum and temperature are held constant for two hours. It is visually possible to see when the solvent has been

**Figure 4.1.** (a) Representative schematic of the swelling of the polymer chains and the formation of the nanofoam upon sublimation of the frozen solvent by freeze drying, and (b) the schematic of the collapse of the nanofoam showing the return of the structure to its original cross-linked shape.
sublimated out of the system as the samples change in color and become opaque. At this point, the temperature is allowed to reach room temperature and then vacuum is released.

### 4.2.3 Exposure of nanofoams to analytes

#### 4.2.3.1 Base layers on silicon wafers

To measure the response of the nanofoams to various analytes, a closed cell containing the system is exposed sequentially to different solvents for 40 minutes each exactly, to allow time for the solvent to evaporate and reach saturation. To fully collapse the layer, it is necessary to expose it to liquid chloroform (original environment) for ten minutes. A schematic of this procedure is shown in Figure 4.1b.

#### 4.2.3.2 Waveguide resonators

Vivek Singh, under the advisory of Anu Agarwal and Lionel Kimerling at MIT, fabricated and tested the microdisk resonators. The optical response of the nanofoam-coated microdisk resonators exposed to various analytes was measured by collecting transmission spectra with a LUNA Optical Vector Analyzer (OVA) at MIT, which included infrared laser source and detector. The measurement setup consisted of tapered lens-tip optical fibers mounted on software-controlled motorized stages with 50 nm motion resolution and a stationary stage on which the sample and analyte were placed. The laser light from the OVA was coupled to the resonator sample with the fibers and the stages automatically aligned to maximize the amount of input and output light at the waveguide facets. The OVA scanned the tunable laser from 1525 nm to 1610 nm with a step size of 1.25 nm and recorded the optical loss in the devices. A reference spectrum without any analyte was collected at first and then another measurement was recorded...
after 32 minutes of analyte exposure. Subsequent analyte exposures were performed after letting the sample dry in air for two hours. For the resonator samples, the same solvents were studied with the addition of isopropyl alcohol.

4.2.4 Characterization techniques

Dry grafted layer thickness was determined by ellipsometry measurements as discussed in Section 3.3.4.1. Swelling and collapsing was studied using in-situ ellipsometry (Section 3.3.4.2) and reflectometry was used to measure the dry layer thickness before and after exposure to analytes as described in Section 3.3.5. AFM (Section 3.3.3) was utilized to study the change in morphology upon exposure to analytes and to monitor the changes in surface structure, as well as porosity, before and after foaming, and upon collapsing.

4.2.5 Equations used to characterize polymer nanofoams

Ellipsometric thickness of all components at particular points on the sample was used to calculate anchored chain density (chains/nm$^2$) of each component as described below. The anchored chain density ($\Sigma$, chains/nm$^2$), i.e., the inverse of the average area per adsorbed chain was determined using Equation 3.1 in Section 3.3.6.

The nanofoam system can be considered a two-component system, where one component is the polymer and the other component is the pores within the polymer matrix, filled with air. The equation for a two-component system is presented in Eq. 4.1 [17]:

\[
 f \left( \frac{n_{\text{dry}}^2 - n^2}{1 + 2n} \right) + p \left( \frac{1 - n_{\text{dry}}^2}{1 + 2n} \right) = 0
\]

\[
 \text{Eq. 4.1}
\]
where $n$ is the effective refractive index to be calculated for any layer, $p$ is the volume fraction of pores, $f=1-p$, the polymer volume fraction, and $n_{\text{dry}}$ is the refractive index of the polymer layer before foaming, calculated Eq. 4.2:

$$n_{\text{dry}} = x_{\text{PGMA}}n_{\text{PGMA}} + x_{\text{PS}}n_{\text{PS}} + x_{\text{EA}}n_{\text{EA}}$$

Eq. 4. 2

where $x_{\text{PGMA}}$, $x_{\text{PS}}$, and $x_{\text{EA}}$ are the volume fractions of PGMA, PS, and EA present in the dry layer, and $n_{\text{PGMA}}$, $n_{\text{PS}}$, and $n_{\text{EA}}$ are the known refractive indices of each component respectively. To note, the refractive index of air was assumed to be 1. The modeling results are compared to simple additive proportional average of the layers, whose generic form is shown in Eq. 4.3.

$$n = x_1\mu_1 + x_2\mu_2 + x_3\mu_3 ...$$

Eq. 4. 3

where $x_i$ is the fraction of component $i$ and $\mu_i$ is the refractive index of component $i$ and so on.

4.2.6 Statistical Analysis on response of nanofoams to analytes

The F-test is one example of a statistical test that determines how unlikely your result to have been, if the two values you compared really were not different. In many areas of science, an arbitrary value of 5% level of probability is used. This implies that the F ratio calculated would happen only 5% of the time if the variances were equal and it is possible to then proceed with the assumption that the variances really are different, and accept a 5% chance of being wrong. It is possible to use a tabulated F value of 0.314 (given 3 degrees of freedom for each population) as the critical value. If the calculated F value is larger, it is possible to reject the notion (known as the null hypothesis, or $H_0$) that the variances are equal, and accept the alternative notion, which is that they are unequal.
If our calculated F value is smaller, there is no evidence to reject the null hypothesis, and would proceed with the assumption that the variances were equal. So, if $F_{\text{calculated}} > F_{\text{critical}}$, $H_0$ is rejected. If $F_{\text{calculated}} < F_{\text{critical}}$, $H_0$ cannot be rejected.

The one-tailed version only tests in one direction. In other words, it determines if the variance from the first population is either greater than or less than (but not both) the second population variance. For example, if testing a new process, you would use a one-tailed test only when interested in knowing if the new process is less variable than the old process.

In terms of analyzing the swelling and collapse data, it is necessary to use a two-tailed test. The F hypothesis for a two tailed test is defined as:

$H_0$: $\sigma_{21} = \sigma_{22}$

$H_a$: $\sigma_{21} \neq \sigma_{22}$

where $\sigma_{21}$ and $\sigma_{22}$ and are the sample variances. The more this ratio deviates from 1, the stronger the evidence for unequal population variances.

4.3 Results and Discussion

4.3.1 Synthesis of EPL base layer

4.3.1.1 Selection and deposition of base layer

Base layers bearing different amounts of epoxy groups were deposited on silicon wafer substrates via dip-coating from a 1% and 2% solution in chloroform, a solvent with high affinity for both base polymers to achieve total solvation. Specifically, poly(glycidyl methacrylate) (PGMA) was selected due to the presence of an epoxy functionality located
in the backbone repeat unit. Poly(methyl methacrylate-ran-glycidyl methacrylate) (PMMA-co-PGMA) was synthesized as described in Chapter 3.2.4, with the intention to achieve an epoxy concentration of 30% compared to that of just PGMA. Extensive work has been published in literature in the last decade on the deposition and characterization of PGMA layers\(^{18,19}\). It was shown that, at maximum, 60% of epoxy groups may be lost due to self-cross-linking of PGMA film during annealing\(^{18,20}\). PGMA and PMMA-co-PGMA were studied as a single EPL because, not only they will be used as the primary component of more complex EPLs, but also due to their own unique chemistry, which can be utilized for targeting multiple analytes.

**Figure 4.2.** Activated silicon wafer surface deposition of PGMA and PMMA-co-PGMA and subsequent cross-linking (annealing).
Figure 4. 2 displays an overall schematic of the film formation technique for the generation of the base layers. After the deposition by dip coating, the polymer layers were annealed under vacuum at 120°C and 150°C for PGMA and 150°C for PMMA-co-PGMA. These conditions were chosen after thorough studies on concentration effects of the polymer in solution on grafted thickness. The ultimate goal was to produce a smooth, uniform layer between 50-100 nm in thickness. To achieve this, different substrates were dip coated in solutions of PGMA of varying concentrations, with the intention of understanding the maximum achievable deposited thickness. The data in Figure 4. 3 reveal the effect of concentration of the polymer in solution on deposited thickness by dip coating, before annealing. The purpose of this was to optimize dip coating conditions to regulate the thickness of the baselayer.

![Deposited Thickness by dip coating (nm) vs. % Concentration](image-url)

**Figure 4. 3.** Deposited layer thickness of PGMA as a function of concentration of polymer in solution.
The next step was to investigate how annealing temperature affects cross-linking of the base layer (and consequently final grafted thickness) for each of the different concentrations. Each deposited layer was annealed overnight (24 hours) at 120°C. After annealing, samples were vigorously rinsed in chloroform to remove excess of non-anchored polymer.

Data from Figure 4.4 reveal a virtually linear dependence between deposited thickness and grafted thickness. From these results, the concentrations of 1% and 2% were hence chosen as they seemed to give the targeted values of 50 and 100 nm, respectively. Atomic Force Microscopy was performed on selected base layers to characterize their morphology. AFM images in Figure 4.5 shows the resulting layers for both PGMA and PMMA-co-PGMA, which were both smooth and uniform in morphology.

![Dependence between deposited thickness and grafted thickness after annealing the deposited polymerfilm. Grafting was achieved at 120°C for 24 hours.](image-url)

**Figure 4.4.** Dependence between deposited thickness and grafted thickness after annealing the deposited polymerfilm. Grafting was achieved at 120°C for 24 hours.
The ultimate objective was to achieve a cross-linked layer that was swellable, but not solvable. Consequently, target annealing temperatures of 120°C and 150°C were investigated to understand the extent of cross-linking density as a function of temperature. It is expected that higher temperatures would lead to higher cross-linking density and, consequently, higher grafted thickness after annealing.

Figure 4.6 shows the change in grafted thickness as a function of temperature and concentration. At temperature of 150°C, the grafting kinetics are slightly faster, resulting in larger grafted thickness. From Figure 4.6, the temperature for PGMA was chosen to be 120°C for 24 hours. Zdyrko et al. had previously shown the existence of a linear trend between time of annealing and grafted thickness. The temperature of annealing for the PMMA-co-PGMA layer was altered to be 150°C as partial de-wetting of the layer was noticed at 120°C. We suggest that de-wetting is connected to lower concentration of epoxy groups. All other conditions (time, concentrations) were left
unaltered. These parameters were chosen as it is believed that the EPL grafted layers have enough cross-linked epoxy groups to be sufficiently cross-linked as to be swellable.

![Graph](image)

**Figure 4.6.** Effect of temperature on grafted thickness for a 2% concentration of PGMA in chloroform. Annealing time was 4 hours.

It is also believed that there are enough non-cross-linked epoxy groups available to utilize for further functionalization. The difference in annealing temperature between the two different EPLs does not affect the results as the time and temperature chosen give the layers with full cross-linking density. The final PGMA and PMMA-co-PGMA layer thickness utilized are shown in Table 4.1. The grafted chain density was calculated using **Equation 3.1** and **3.2** in Section 3.3.6. The grafted chain density appears to increase as thickness increases for both PGMA and PMMA-co-PGMA. For similar values of
thickness, the grafted chain density is comparable between PGMA and PMMA-co-

PGMA.

Table 4.1. Grafted chain density calculations based on the average grafted thickness for PGMA and PMMA-co-

PGMA.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness (nm)</th>
<th>Grafted Chain density (chains/nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>53.3±1.5</td>
<td>0.202±0.006</td>
</tr>
<tr>
<td></td>
<td>126.3±8.0</td>
<td>0.478±0.030</td>
</tr>
<tr>
<td>PMMA-co-PGMA</td>
<td>44.7±3.5</td>
<td>0.207±0.016</td>
</tr>
<tr>
<td></td>
<td>98.4±4.5</td>
<td>0.457±0.021</td>
</tr>
</tbody>
</table>

4.3.1.2 Swelling behavior of the EPL base layer to selected solvents

The chemical groups along the backbone of the EPL polymer chain are capable of dispersive, polar, and hydrogen bonding. These interactions will determine what solvents are most suitable for swelling the polymer (i.e. a stronger response to the analyte). In the presence of a solvent for which the polymer chain has a strong affinity, the chain will become significantly extended. The interaction between the EPLs and the analytes can be quantified by use of the solubility parameters. The solubility parameter can be used to estimate how well an analyte will be absorbed by a polymer film. The strength of the interaction (affinity) is determined by how similar the solubility parameters of the analyte and of the EPL are in values.

A solubility parameter approach proposed by Hansen is called the Hansen Solubility Parameter (HSP).²¹ The basis of HSPs is that the total energy of vaporization of a liquid consists of several individual parts: dispersion forces, permanent dipole–
permanent dipole forces, and hydrogen bonding. The total cohesive energy, $E$, can be measured by breaking all the physical bonds, such as by evaporating the liquid. Consequently, the total cohesive energy is the energy of vaporization, which implies that materials with similar HSP have high affinity for each other. \textsuperscript{21} \textbf{Eq. 4. 4} represents the basic equation governing the HSP:

$$E = E_D + E_P + E_H$$ \textbf{Eq. 4.4}

where $E_D$, $E_P$, and $E_H$ are the dispersive, dipole-dipole, and hydrogen energy components. \textsuperscript{21} When \textbf{Eq. 4. 4} is divided by the molar volume ($V$), it is transformed into \textbf{Eq. 4. 5}.

$$\delta = \delta_D + \delta_P + \delta_H$$ \textbf{Eq. 4. 5}

where $\delta$ is the Hansen solubility parameter, as the sum of the square of each component for dispersive, polar, and hydrogen energies. The customary equation to calculate the solubility parameter “distance”, $Ra$, from the partial solubility parameters is:

$$Ra^2 = 4\left(\delta_{D_2} - \delta_{D_1}\right)^2 + \left(\delta_{P_2} - \delta_{P_1}\right)^2 + \left(\delta_{H_2} - \delta_{H_1}\right)^2$$ \textbf{Eq. 4. 6}

where $\delta$ is the Hansen solubility parameter for the solvent (1) and polymer (2), and D, H, and P stand for dispersive, hydrogen, and polar forces. The “4” in front of the dispersive forces components was found empirically useful for plotting. $Ra$ is a measure of the interaction between polymer and solvent; smaller $Ra$ values represent better interactions. Reliable $Ra$ values for numerous solvents and polymer can be used to determine the $Ra$ for the polymer, in the same manner as swelling data is being used for a similar purpose. \textsuperscript{21} \textbf{Table 4. 2} presents known and calculated HSP values for PMMA and PGMA polymers.
Table 4.2. Partial solubility parameter values for PGMA and PMMA, and the calculated partial solubility parameter for PMMA-co-PGMA.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta_D$(MPa)</th>
<th>$\delta_P$(MPa)</th>
<th>$\delta_H$(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA (Ref. 22)</td>
<td>18.6</td>
<td>10.5</td>
<td>5.1</td>
</tr>
<tr>
<td>PGMA (Ref. 22)</td>
<td>16.5</td>
<td>7.6</td>
<td>9.2</td>
</tr>
<tr>
<td>PMMA-co-PGMA (Eq. 4.7)</td>
<td>17.9</td>
<td>9.6</td>
<td>6.3</td>
</tr>
</tbody>
</table>

From Table 4.2, it is possible to take the weighted average of each component (PMMA and PGMA) knowing that the copolymer is 70:30 in ratio, and calculate the HSP value for PMMA-co-PGMA using Eq. 4.7 below:

$$\delta_{PMMA-co-PGMA} = \mu_{PMMA}\delta_{PMMA} + \mu_{PGMA}\delta_{PGMA}$$  \hspace{1cm} \text{Eq. 4.7}

where $\mu_{PMMA-co-PGMA}$ and $\mu_{PGMA}$ are the fractions of PMMA-co-PGMA and PGMA respectively (70:30). The components for various solvents are presented in Table 4.3.

Table 4.3. Hansen Solubility Parameters for the Solvent Included. \(^{21}\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>15.1</td>
<td>12.3</td>
<td>22.3</td>
</tr>
</tbody>
</table>

From Table 4.3 the $(Ra)^2$ for PGMA and PMMA-co-PGMA with the respective solvent affinities (acetone, toluene, chloroform, and methanol) can be calculated using Eq. 4.6, and are presented in Table 4.3 below.

Table 4.3. Calculated $Ra^2$ values for PGMA and PMMA-co-PGMA systems used with the respective solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PGMA</th>
<th>PMMA-co-PGMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>16.68</td>
<td>25.44</td>
</tr>
<tr>
<td>Toluene</td>
<td>99.28</td>
<td>86.48</td>
</tr>
<tr>
<td>Chloroform</td>
<td>39.26</td>
<td>43.15</td>
</tr>
<tr>
<td>Methanol</td>
<td>201.54</td>
<td>295.12</td>
</tr>
</tbody>
</table>
From Table 4.3 it is possible to notice two distinct trends. The polymer-solvent systems involving acetone and chloroform have distinctly lower $R_a^2$ values (better solubility with PGMA and PMMA-co-PGMA) than polymer-solvent systems involving toluene and methanol. Consequently, the four solvents were selected and used as they produced thermodynamic systems with a good range of solubility.

The swelling extent was measured for 50nm thick films of PGMA and of PMMA-co-PGMA that were individually exposed to: acetone, toluene, chloroform, and methanol. Three samples were measured for each solvent. The values of swelling for each EPL and for each solvent are presented in Figure 4.7. The swelling ratio is determined as:

$$Swelling \ Ratio = \frac{d}{d_0}$$

where $d$ is the final thickness of the swollen film from the dry state and $d_0$ is the film’s dry initial state thickness.

Because PMMA and PGMA have very similar molecular structures, it is understandable to see similar swelling values and similar interaction trends. In fact, the extent of swelling from Figure 4.7a and Figure 4.7b shows a similar trend as compared to the affinity between the solubility parameters of the solvents and the polymers (Table 4.2 and Table 4.3).
Figure 4.7. PGMA EPL swelling (a) and PMMA-co-PGMA EPL swelling(b).
In fact, acetone and chloroform swell both the PGMA and the PMMA-co-PGMA systems to a much larger extent than toluene and methanol, corresponding to the estimated $Ra^2$ values for the polymer-solvent systems. Interestingly enough, chloroform swells the materials more although the estimated $Ra^2$ value is higher than that of acetone. It is hypothesized that this difference in trend could be due to different reasons. The main reason is that the Hansen solubility parameter is an estimate for solubility and not swellability. In addition, it estimates solubility for polymers in a solvent whose chains are not tethered to a surface and are not cross-linked, as in the case of the polymeric base layers. Another reason for the deviation is that the PGMA epoxy groups are open because of cross-linking, which changes the structure of the chain and consequently solvent affinity. Due to these reasons, it is possible to explain how the order of affinity for swellability for PGMA base layer systems is chloroform, acetone, toluene, methanol, whereas the order of affinity for PMMA-co-PGMA is chloroform, acetone, methanol, and toluene.

Chloroform was selected as the solvent to be used during the foaming procedure, since it allowed for the largest extent of swelling. It was hypothesized that a larger extent of foaming would result in a stronger interaction with the various analytes. Such an effective interaction would, in turn, correspond to a larger extent of response and consequently, the most efficient targeting of analytes.

Another possible way of calculating thermodynamic affinity of polymer-solvent pairs is by using the Flory-Huggins “chi” parameter. The Flory-Huggins “chi” parameter, $\chi_{12}$, has been used for many years in connection with polymer solution
behavior, where 1 and 2 represent the solvent and polymer respectively. Specifically, **Equation 4.9** is used to find the value for the interaction parameter from swelling experiments.

\[
\chi = \frac{-\left(\ln(1 - \phi_2)\right) - \phi_2 - \frac{\rho V}{M_c} \phi_2^{-1/3}}{\phi_2^{1/3}}
\]

where \(\phi_2\) is the volume fraction of the polymer, \(\rho\) is the material density, \(V_1\) is solvent volume, and \(M_c\) is the molecular weight between cross-links. This approximation provides a good qualitative comparison for polymer-solvent pairs with regard to the affinity of the solvent to the system and the cross linked/grafted sites.\textsuperscript{22} Using swelling data of the polymer films, it is possible to determine polymer–solvent interaction parameters to describe polymer-solvent pairs based on known parameters. Additional experiments would be performed to determine the molecular weight between cross-link points, as well as the volume of the solvent to calculate “chi” interaction parameters for all the systems investigated in this dissertation.

### 4.3.2 Foaming of EPL base layers

#### 4.3.2.1 Thickness and characterization of foamed EPL base layers

The fabrication of shape memory polymer nanofoams was successful with both PGMA and PMMA-co-PGMA polymers. For a 53.3±5.3nm PGMA film, the average foamed thickness was 20.2±4.9%. For 127.1±11.3nm films of PGMA the average foaming was 12.6±2.5%. It can be noted that thinner films foamed more than thicker films indicating lower level of cross-linking (**Table 4.1**).
Table 4.4. Foaming and collapsing of shape memory PGMA, with included grafted chain density for different thicknesses.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness (nm)</th>
<th>Foam (%)</th>
<th>Collapse (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>53.3±1.5</td>
<td>20.2±4.9</td>
<td>99±1</td>
</tr>
<tr>
<td></td>
<td>126.3±8.0</td>
<td>12.6±2.5</td>
<td>99±1</td>
</tr>
</tbody>
</table>

Table 4.4 also presents that when the EPL foams were exposed to their original environment, they collapsed and returned to their original thickness within a 1% error.

Figure 4.8 shows AFM images of the foamed and collapsed PGMA layers revealing their shape memory properties. The AFM images show that the PGMA, upon foaming, has a significant porosity.

![AFM images of the foamed and collapsed PGMA foams revealing their shape memory properties.](image)

Figure 4.8. AFM images of the foamed and collapsed PGMA foams revealing their shape memory properties. The AFM images reveal that the PGMA, upon foaming, has a uniform porosity. All images are 1x1µm; Z height: 25nm.

The fabrication of shape memory polymer nanofoams was successful with PMMA-co-PGMA polymer as well. The PMMA-co-PGMA films of 41.9±1.9nm foamed on average 34.8±7.8%, whereas the thicker films of 98.4±6.3nm foamed 24.6±3.5%. The copolymer foamed to a larger extent compared to the PGMA. This is most likely due to
the fact that fewer epoxy groups are present in the copolymer, and consequently allow for much less cross-linked system, capable of swelling to a larger extent. When the foams were exposed to their original environment, they collapsed and returned to their original thickness within a 1% error (Table 4.5).

Table 4.5. Foaming and collapsing of shape memory PMMA-co-PGMA, with included grafted chain density for different thicknesses.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Thickness (nm)</th>
<th>Foam (%)</th>
<th>Collapse (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-co-PGMA</td>
<td>44.7±3.5</td>
<td>34.8±7.8</td>
<td>99±1</td>
</tr>
<tr>
<td></td>
<td>98.4±4.5</td>
<td>24.6±3.5</td>
<td>99±1</td>
</tr>
</tbody>
</table>

Figure 4.9 shows AFM images of the foamed and collapsed PMMA-co-PGMA system revealing their shape memory properties. The AFM images reveal that the copolymer, upon foaming, has a much larger and uniform porosity than for PGMA due to the larger extent of foaming.

Figure 4.9. AFM images of the foamed and collapsed PMMA-co-PGMA system revealing their shape memory properties. The AFM images reveal that the copolymer, upon foaming, has a much larger and uniform porosity than for PGMA due to the larger extent of foaming. All images are 1x1µm; Z height:25nm.
In general, it appears that with decreasing cross-linking density there is an increase in the foaming percent. PMMA-co-PGMA foams to a larger extent than PGMA. In general, it appears that thinner films foam to a larger extent.

4.3.2.2 Porosity

Nanotomography was utilized to analyze the inner structure of the PGMA film after solvent sublimation to confirm that the PGMA grafted nanofoam had pores throughout the film. The approach consisted in a step-by-step air plasma etching of the film with a subsequent step-by-step AFM analysis of the etched surface, to reveal the inner morphology.

Figure 4.10. (a) Change in thickness measurements were used to track the etched polymer film after each step and (b) simultaneous reference experiment was conducted with the nonporous PGMA film. All images are 1x1µm. Images produced by Yuriy Galabura.
Change in thickness measurements were used to track the etched polymer film after each step (Figure 4. 10a). Simultaneously, a reference experiment was conducted with the nonporous PGMA film. Results are presented in Figure 4. 10b. AFM imaging revealed that, in fact, pores were situated not only on the surface but also throughout the PGMA foamed layer. Imaging of the nonfoamed plasma-etched PGMA film clearly demonstrated that the observed porous structure was not an artifact caused by plasma etching. The size of the interconnected and open pores inside the film was estimated to be between 10 and 100 nm.

4.3.2.3 Response to Analytes

The interaction of the foamed polymer systems with saturated vapor of four solvents of different nature was studied. The interaction was achieved by swelling the layers for 40 minutes in saturated vapor solvent, monitoring the extent of swelling before and after foaming, and measuring the percent collapse after the 40 minute exposure.

The swelling extents of before and after foaming are presented in Figure 4. 11a for PGMA and in Figure 4. 11b for PMMA-co-PGMA. The “before” graphs are reproduced from Figure 4. 7 a-b for ease of comparison of results between swelling before and after foaming. The foamed structures do appear to swell to a larger extent than the collapsed layers (before foaming) for both polymers and for all solvents. This can be due to two possible reasons. The first reason could be that the foamed samples are not actually foamed to their maximum extent. The chains undergo a temperature transition from -90°C to room temperature which could cause a partial relaxation of the chains. The other explanation could be that when a sample is foamed it has a much larger surface area
for the saturated vapor analyte to interact with the chains compared to a film in a collapsed state (before foaming). This could conclude that, in the collapsed state, the swelling does not reach a saturated vapor equilibrium condition to allow for a maximum swelling extent. From Figure 4.11 it can be seen that selected solvents for the system (acetone and chloroform) allow for a much larger extent in swelling (before and after foaming) than non-selective solvents (methanol and toluene), concluding that the base layer shows imparted selectivity to different analytes.

Figure 4.12a and Figure 4.12b present the percent collapse that each system underwent after being exposed to saturated vapor. As expected, selective solvents collapsed the system more than non-selective solvents like methanol, due to the different thermodynamic affinity as shown in Table 4.1 and Table 4.2. Chloroform vapor, being the closest analyte to the original environment the SMP was formed in (liquid chloroform) causes the largest extent of collapse. It consequently appears that the SMP can differentiate between phases (vapor or liquid) of the same analyte.
Figure 4.11. Swelling response for each analyte in saturated vapor conditions before and after foaming for (a) PGMA films and (b) PMMA-co-PGMA films.
Figure 4.12. Percent collapse of the individual response after exposure to each analyte for (a) PGMA films and (b) PMMA-co-PGMA films.
An F-test with a 95% confidence interval (Section 4.2.6) was performed to reveal if there is a statistical significance between the variances in the extent of collapse produced by acetone, toluene, chloroform, and methanol for either PGMA or PMMA-co-PGMA. The results are presented in Table 4.6.

**Table 4.6.** Calculated F-values for the collapse of PGMA and PMMA-co-PGMA systems with each analyte and comparing the significance of collapse for the same solvent for PGMA versus PMMA-co-PGMA.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Acetone</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>2.4</td>
<td>0.042</td>
<td>1.86</td>
<td>0.53</td>
</tr>
<tr>
<td>Copolymer</td>
<td>4</td>
<td>0.157</td>
<td>2.71</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Values above $F_{95}=0.314$ reveal that within a 95% confidence, the collapse results are statistically significant, implying that the system can in effect detect the analyte and the resulting change in thickness is, in effect, a result of the exposure to the analyte. For example, the collapse seen as a function of acetone can be said to be statistically significant. On the other hand, it cannot be concluded (within 95% confidence) that the PGMA collapse as a function of toluene is significant, implying that the decrease in thickness could be due to simple plasticization of the film in the presence of the analyte (and not a true “detection”, like with acetone).

In addition, the same F-test was performed to compare the percent collapse of PGMA with PMMA-co-PGMA for each analyte. The results are presented in Table 4.7.

**Table 4.7.** Calculated F-values for the collapse of PGMA and PMMA-co-PGMA systems with each analyte and comparing the significance of collapse between PGMA versus PMMA-co-PGMA.

<table>
<thead>
<tr>
<th>Polymer Vs.</th>
<th>Acetone</th>
<th>Toluene</th>
<th>Chloroform</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>0.57</td>
<td>0.013</td>
<td>0.112</td>
<td>0.571</td>
</tr>
<tr>
<td>Copolymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
From data in Table 4.6 and Table 4.7 it can be seen that there were systems that showed no significant difference in the extent of response. Such systems included all the ones that involved exposure to toluene, signifying that neither base layer has a strong affinity with this analyte, which corresponds to the larger $Ra^2$ values calculated for base layer-toluene systems. This trend is similar to methanol and its interactions with PGMA and PMMA-co-PGMA. The base layers exposed to acetone (PGMA-Acetone and PMMA-co-PGMA-Acetone) showed $F_{95}>0.314$ values, implying that there was strong affinity between each of the base layers and acetone, again in accordance with calculated $Ra^2$ values for those systems. The F-value that compares the interaction between PGMA-acetone and PMMA-co-PGMA-acetone is less than 0.314. This means that acetone does not differentiate between the base layers. A similar trend occurs with chloroform.

Generally, it can be concluded that the system can differentiate between “good” solvents (Acetone and chloroform) with statistical significance. It cannot be concluded though that the system can differentiate with statistical significance the response to “bad” solvents.

4.3.2.4 Refractive Index Calculations

The polymer foams are ultimately be placed on wave-guides that measure the change in propagation of light upon collapsing of the foam as an analyte is being sensed. Consequently, it is of importance to understand if the extent of response the foams is significant to be able to detect a change in refractive index. The extent of response in terms of change in thickness and morphology of the PGMA foams was significant for all systems. For our calculations, we used literature values presented in Table 4.8.
Table 4.8. Literature values for PGMA and air used for the Bruggeman model and the simple average calculations for Refractive index for PMMA-co-PGMA from Eq. 4.2.

<table>
<thead>
<tr>
<th></th>
<th>PGMA</th>
<th>PMMA-co-PGMA</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1.5</td>
<td>1.493 (Eq. 4.2)</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.13 represents the changes in refractive index ($\lambda$=651nm) as a function of normalized change in thickness for PGMA (Figure 4.13a) and PMMA-co-PGMA (Figure 4.13b). Data in Figure 4.13 reveals that both models of refractive index give very similar values for refractive index for all systems. As expected, as the polymer film foams, the porosity increases and consequently the refractive index decreases. In contrast, as the foamed layer collapses in sequential manner to each analyte, the refractive index starts increasing. When exposed to the original environment of chloroform liquid, both thickness and refractive index go back to their initial value.
Figure 4.13. Change in refractive index as a function of change in thickness upon sequential exposure to various analytes for (a) PGMA films and (b) PMMA-co-PGMA films.
It appears that in PMMA-co-PGMA systems, the change in refractive index as a function of change in thickness is much larger than for PGMA systems. This leads to the conclusion that PMMA-co-PGMA systems are much more sensitive to the environment and that it is possible to detect changes in refractive index for any system, which is important for the waveguide resonators detection platform.

4.3.2.5 Waveguide Track Resonators

4.3.2.5.1 Fabrication of amorphous silicon resonators

The fabrication of the amorphous silicon resonator devices was done at MIT, by Vivek Raghunathan. Detection mechanisms for such devices are based on shifting of light wavelength based on changes local refractive indices caused by analyte incorporation into the polymer film or absorption of the light by the penetrating vapor. 23

4.3.2.5.2 EPL nanofoams’ response on waveguide track resonators

The nanofoams on the resonators were exposed to different analytes and the response are shown in Figure 4.14 a-b. The PGMA system tested reveals very particular and distinct responses. Interestingly enough, not all systems show a shift towards higher wavelengths upon exposure to analytes. A shift towards higher wavelengths corresponds to an increase in refractive index, which is what is expected as the foams partially collapse. The resonators showed that the detection platform was successful.
Figure 4.14. Optical response of micro disk resonators covered with nanofoams layers post-exposure to different analytes. (a) PGMA nanofoam (b) PMMA-co-PGMA nanofoam
The fact that the copolymer shows a different trend than PGMA signifies that there is a different mechanism upon collapsing that occurs when the chains relax. It is hypothesized that upon collapsing the pores in the copolymer merge. This can be confirmed by the fact that for PMMA-co-PGMA responses, the shifts in wavelength change direction. In fact, if the pores coalesce upon collapsing, light of specific wavelengths can pass through easier than if the pores had diminished in diameter.24 The resonators showed that the detection platform was successful.

4.4 Conclusions

The fabrication of shape memory polymer nanofoams was successful with both PGMA and PMMA-co-PGMA polymer EPLs. The copolymer foamed to a larger extent compared to PGMA. The nanofoams revealed shape memory behavior due to the fact that, when exposed to their original environment, they collapsed and returned to their original thickness within 1% of their original value. AFM images reveal the change in morphology upon foaming, as well as the presence of uniform pores throughout the nanofoam.

The foamed EPL structures appear to swell to a larger extent than before foaming for both polymers and for all solvents analyzed. This phenomenon can be explained by the simple conclusion that the samples are not actually foamed to their maximum extent. Another possible explanation for this event is that upon foaming, there is added surface area due to the presence of pores. This, consequently, could conclude that, in the
collapsed state, the swelling does not reach a saturated vapor equilibrium condition to allow for a maximum swelling extent.

Selected solvents for the system (acetone and chloroform) swell the layers to a much larger extent than non-selective solvents (methanol and toluene), as expected. Consequently, the base layer reveals an imparted selectivity to various analytes. Similarly, selective solvents collapsed the system to a larger extent than non-selective solvents. The largest extent of collapse is seen with chloroform vapor as it is the closest analyte to the original environment.

Due to the fact that the change in refractive index is large, the resonators proved to be a successful detection platform. In addition, the copolymer shows a different trend in light absorption than PGMA, which implies that upon collapsing the pores in the copolymer merge.

Chapter 4 shows that shape memory nanofoams with imparted selectivity to various analytes can be produced. The changes in thickness, morphology, and refractive index are successful methods to monitor the response of the shape memory nanofoam. Finally, this new platform can be used for further functionalization to impart selectivity and specificity so as to create a very sensitive and efficient sensor, capable of identifying and remembering multiple environments.
4.5 References


5 CHEMICAL MODIFICATION OF NANOFOAM FILMS

5.1 Introduction

Chapter 4 describes the synthesis and behavior of nanofoam films made of PGMA and PMMA-co-PGMA. It was shown that nanofoam EPLs with shape memory properties can be used as a detection tool. It was also shown that the Hansen interaction parameter is a useful tool to estimate the specificity and selectivity of the system. Due to the fact that PGMA and PMMA-co-PGMA are very similar in chemical structure, the detection parameters and response to the detection of both base layers is very similar in nature. Consequently, to further tune the specificity of the EPLs produced in Chapter 4, it is necessary to be able to change the interaction parameter so that the shape memory EPLs can be sensitive to different chemicals. This can be achieved by introducing different chemical moieties that can target different analytes.

The introduction of chemical functionalities in polymer layers can be achieved in a number of ways. For instance, grafting of polymers is currently a widely used method for synthesis, modification, and functionalization of nano-scale films including the stimuli responsive ones. 1-3 End-functionalized polymer chains may be grafted to the solid substrate (grafting to) or the grafting reaction can proceed by polymerization from the surface (grafting from). 3 Grafting can be used as a method to impart functionalities specific to a target analyte. The “grafting to” technique involves reaction of functionalized polymer chains with the (complementary) functional groups located on the surface, resulting in the formation of tethered chains. 1, 2, 4 One of the major advantages
of the “grafting to” method is that the polymer used can be characterized, functionalized and treated in various ways before reacting it with the surface of the substrate. In addition, different molecular weight and polydispersity polymers can be used, although polymers with a narrow molecular weight distribution produce better defined brushes. On the other hand, “grafting from” involves polymerization that is initiated at the substrate surface by attached (usually covalently bonded) initiating groups.\textsuperscript{3, 4} Most of the time, the immobilization of the initiators requires multiple steps, which may lead to low graft densities of initiators. Consequently, to be able to add chemical moieties to the layer to tune the interaction parameter to produce a shape memory EPL that shows imparted specificity and selectivity, the “grafting-to” method was employed for this work.

To this end, the primary focus of \textbf{Chapter 5} is the chemical functionalization of the shape memory nanofoams described in \textbf{Chapter 4}. By chemically functionalizing the SMPs, it is expected that the system will show added specificity and selectivity to various chemical substances. In other words, \textbf{Chapter 5} will describe the fabrication and characterization of shape memory nanofoams with the added chemical components.

The chemical functionalization needed to add functionality throughout the nanofoam, and not just be limited to the surface. For this purpose, low molecular weight polymer such as carboxy-terminated polystyrene (PS-COOH) and molecules, such as ethanol amine (EA) were used. Such substances can penetrate the cross-linked base layer, swell the system and react within the base layer and not just on the surface. The chemically functionalized base layers were successfully foamed and show specificity and selectivity to different analytes. Four solvents with varying affinities to the chemical
functionalities were used as target analytes in both their vapor and liquid phases. The different chemical functionalities interact selectively to the analyte present. The analytes act as plasticizers, causing a localized relaxation (partial collapse) of the foamed structure where that functionality is present. In addition, the chemically functionalized nanofoam EPLs show typical characteristics of shape memory materials as they collapse when re-introduced to their original environment. Reflectometry and atomic force microscopy were used to monitor the changes in thickness and morphology of the chemically functionalized shape memory nanofoams.

5.2 Experimental

5.2.1 Carboxy-terminated polystyrene

Deposition of carboxy-terminated PS film for grafting is achieved by dip coating PGMA or PMMA-co-PGMA films from a 2% solution of polystyrene with added 30% w/w of non-terminated high molecular weight polystyrene (M<sub>n</sub>=300,000 g/mol) from chloroform. The samples are annealed at 150°C for four hours. After annealing, the samples are rinsed in chloroform three times for thirty minutes, with solvent replacement every thirty minutes.

5.2.2 Ethanol amine

Ethanol amine (EA) is introduced into PGMA or PMMA-co-PGMA films from a 2.5% solution in chloroform. The samples remained in the EA solution at 35°C for four hours to graft to the base layers. The samples are then rinsed in chloroform using the same rinsing procedure as for the base layers.
5.2.3 Characterization techniques

Both the PS-functionalized and EA-functionalized films are then treated and characterized in the same way. The samples are foamed as described in Section 4.2.3. The chemically functionalized base layers are exposed to analytes as described in Section 4.2.4. All the samples are characterized using the techniques discussed in Section 4.2.5. The refractive index change upon exposure to analytes is calculated using Equation 4.1. Statistical analysis is achieved as described in Section 4.2.7.

5.2.4 Analysis techniques

Both the PS-functionalized and EA-functionalized films analyzed the same way. The refractive index change upon exposure to analytes is calculated using Equation 4.1. Statistical analysis is achieved as described in Section 4.2.7.

5.3 Results and Discussion

5.3.1 Fabrication of chemically functionalized shape memory nanofoam

Given the versatile chemistry that the PGMA epoxy groups offer, the selection of molecules and macromolecules to use as functionalization options of the EPLs was investigated. One important parameter for the efficiency of the detection mechanism in the design is that the (macro)molecules need to penetrate into the EPL. Penetration is necessary to increase the concentration of that specific functionality to augment the extent of response to the target analytes. In fact, it has previously been shown that higher molecular weight substances are not capable of diffusing into the polymer layer and only
graft on the surface. [11] Consequently, the molecules and the macromolecules of choice are of low molecular weight so as to penetrate the layer.

5.3.1.1 Functionalization with carboxy-terminated polystyrene

Carboxy-terminated polystyrene of a low molecular weight ($M_n = 2,400 \text{ g/mol}$) substance that was used for the functionalization. The carboxy groups at the end of the polystyrene polymer chain react with the unreacted epoxy groups of the PGMA in the base layers. Extensive work had previously been done by Iyer et al. to understand the grafting kinetics of polystyrene with PGMA.\(^5\)

Preliminary grafting was investigated after annealing a film deposited from a 2% solution of carboxy-terminated polystyrene in chloroform at differing temperatures. The glass transition temperature for PS-COOH of $M_w = 2,400 \text{ g/mol}$ is 79°C (Polymer Source, Inc.) The $T_g$ of PGMA is ~70°C for $M_w = 175,000 \text{ g/mol}$ (Polymer Source, Inc.) The temperatures chosen were from 85°C (above the $T_g$, to allow diffusion of the PS-COOH chains in the PGMA matrix) to a high temperature of 175°C. Any chemical reaction is dependent on temperature. Consequently, the higher the temperature results in a higher extent of grafting. The resulting film morphologies of the PS-COOH grafted to the PGMA base layers at the various temperatures is shown in Figure 5.1.
Images in Figure 5.1 reveal that at all temperatures the surface of the PS-COOH film appears to experience de-wetting. Consequently, the film does not appear uniform in nature. To prevent de-wetting from happening, 30% w/v of non-terminated high molecular weight PS ($M_w=300,000$ g/mol) was added to the 2% solution of PS-COOH. The principle behind this method is simple: larger polymer molecules make a solution more viscous than small ones do. In fact, the equation relating melt viscosity and molecular weight of entangled linear polymers can be described with a power law, $\eta \propto M_w^3$. Consequently, a 30% increase in concentration using a $M_w$ 100 times larger than the original $M_w$ of 2,400 g/mol increased the viscosity by $10^4$ times. Consequently, the higher viscosity would minimize flow, in turn reducing (eliminating) de-wetting of
the surface. To conquer dewetting, consequently, a solution of 2% carboxy-terminated PS-COOH with an added 30% w/w of non-terminated polystyrene (M_w=300,000 g/mol) from chloroform was used to deposit the layer on PGMA. The grafting thickness and morphology as a function of temperature was investigated. The lower limit of the temperature was chosen to be 85°C, a value larger than the T_g of PS (T_g =79°C), since grafting does not occur below the glass transition of the polymer.

Data in Figure 5.2 shows the amount of PS-COOH grafted in two hours to a 80 nm PGMA film. Annealing was done for two hours.

Figure 5.2. Relationship between grafting temperature and grafted thickness on an 80 nm PGMA film. Annealing was done for two hours.

Data in Figure 5.2 shows the amount of PS-COOH grafted in two hours to a 80 nm PGMA film. It can be concluded that the PS-COOH does penetrate the chain as it was previously proven by Iyer et al. that higher molecular weight PS-COOH only grafts up to 20 nm on the PGMA film surface. [18] Consequently, the fact that an amount larger than 10 nm was grafted implies interpenetration, as needed to increase the concentration of the functionalization throughout the EPL. A temperature of 150°C (for two hours of
annealing) produced a grafted thickness of 45 nm. Consequently, to achieve a target grafted layer of PS-COOH on the base layer of ~90 nm, the annealing time was increased to 4 hours. With the finalized parameter, PS-COOH was grafted to “thin” (45 nm) and “thick” (100 nm) PGMA films. On thin PGMA films, the average grafted PS thickness was of 65.8±6.0nm and on thick PGMA films 48.2±4.2nm were grafted. “Thin” (50 nm) and “thick” (90 nm) copolymer base layers had 87.6±9.0nm and 130.5±6.4nm of grafted PS, respectively. AFM was performed to analyze the morphology to confirm that there was no dewetting on the surface of the films. Figure 5.3 shows that dewetting was conquered and PS layers at both 120°C (Figure 5.3a) and 150°C (Figure 5.3b) resulted uniform.

After these preliminary results, the final parameters for the functionalization of the PGMA EPL and the PMMA-co-PGMA EPLS were finalized and presented Table 5.
Table 5.1. Grafting parameters for optimal film formation of PS-COOH interpenetrating layer in PGMA EPL and PMMA-co-PGMA EPL.

<table>
<thead>
<tr>
<th>Time Grafted</th>
<th>Temperature (°C)</th>
<th>PS-COOH Mn (g/mol)</th>
<th>PS-COOH concentration (%)</th>
<th>Solvent Used</th>
<th>Added high molecular weight PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>150</td>
<td>2,400</td>
<td>2</td>
<td>Chloroform</td>
<td>30% w/v</td>
</tr>
</tbody>
</table>

5.3.1.2 Functionalization with ethanol amine

Ethanol amine was investigated for functionalization of the base layers. Ethanol amine is a small molecule with a high probability of interpenetration in the EPLs. The amine groups of the ethanol amine molecule react with the epoxy groups of the base layers. The grafting kinetics on PGMA films were investigated for a 2.5% concentration of ethanol amine in chloroform both in the vapor and in the liquid phase at 35°C, with the purpose of understanding the optimal parameters for a uniform film with a certain thickness.

Data in Figure 5.4 reveal that the rate of grafting of ethanol amine to PGMA is faster in the vapor phase than in solution. This can be explained as in the vapor phase the rate of diffusion is higher than in solution. Nevertheless, it appears that within a couple of hours a controllable layer thickness of 20 nm can be grafted within the PGMA EPL. Consequently, the grafting conditions were established to be from solution, at 35°C, for four hours. Thin PGMA-EA foamed 5.8±0.2% while thicker films foamed 9.78±0.4%. On thin PGMA films, the average grafted EA thickness was of 3.9±0.92nm and on thick PGMA films 11.0±1.23nm were grafted. AFM was used to investigate if the established conditions resulted in a uniform smooth film.
Figure 5.4. Kinetics at 35°C of grafting of ethanol amine (2.5% concentration from chloroform) on PGMA from solution and from vapor.

Figure 5.5. AFM image of the morphology of (a) PGMA and (b) of ethanol amine grafted to PGMA at 35°C for 4 hours from solution, resulting in a uniform film. All images have a Z height of 15 nm and are µmx1µm.

Images in Figure 5.5 reveal a change in morphology due to the added thickness of ethanol amine thickness to the original PGMA layer. In addition, the film appears smooth.
and uniform, confirming that the parameters chosen for our chemical functionalization were met.

5.3.2 Swelling behavior of the EPL base layer to selected solvents

As determined in Chapter 4, the chemistry along the backbone of the EPL polymer chain are capable of dispersive, polar, and hydrogen bonding. In the case of the chemically functionalized EPLs investigated in here, the interactions are expected to be altered. For example, in the case of an EPL functionalized with PS-COOH, it is expected that the strength of the interaction with toluene would be much larger than a non-functionalized EPL, due to the fact it is well known that toluene shows great affinity to polystyrene. Similarly to Chapter 4, these interactions will determine what solvents are most suitable for swelling the polymer (i.e. a stronger response to the analyte). Consequently, the strength of the interaction (affinity) is determined by how similar the solubility parameters of the analyte and of the chemical functionality of the EPL are in values.

It is possible, as in Chapter 4, to calculate the $R_{ai}^2$ value for the PGMA-PS systems and for PMMA-co-PGMA-PS systems. The Hansen solubility parameters for polystyrene and ethanol amine are presented in Table 5.2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta_D$(MPa)</th>
<th>$\delta_P$(MPa)</th>
<th>$\delta_H$(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>21.3</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>Ethanol amine</td>
<td>17</td>
<td>15.5</td>
<td>21.2</td>
</tr>
</tbody>
</table>
Using the average grafted thickness, it is possible to estimate the Hansen solubility values for thin (50 nm) and thicker (90 nm) PGMA and PMMA-co-PGMA films using Equation 5.1.

\[ \delta_{\text{Tot}} = \mu_A \delta_A + \mu_B \delta_B \]  

Eq. 5.1

where \(A\) is the base layer, \(B\) is the value for either polystyrene or ethanol amine, and \(\mu\) is the thickness fraction of each respective component. The Hansen solubility parameters for each of the systems are presented in Table 5.3.

The calculated \(R^2\) values for the polystyrene systems interacting with the solvents are presented in Table 5.4.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thin PGMA+PS</th>
<th>Thick PGMA+PS</th>
<th>Thin Copolymer+PS</th>
<th>Thick Copolymer+PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\hat{\delta}_D, \text{Tot})</td>
<td>19.23</td>
<td>18.12</td>
<td>20.09</td>
<td>19.90</td>
</tr>
<tr>
<td>(\hat{\delta}_P, \text{Tot})</td>
<td>6.58</td>
<td>6.99</td>
<td>7.19</td>
<td>7.41</td>
</tr>
<tr>
<td>(\hat{\delta}_H, \text{Tot})</td>
<td>6.42</td>
<td>7.55</td>
<td>5.04</td>
<td>5.16</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thin PGMA+PS</th>
<th>Thick PGMA+PS</th>
<th>Thin Copolymer+PS</th>
<th>Thick Copolymer+PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>70.53</td>
<td>39.27</td>
<td>98.42</td>
<td>89.66</td>
</tr>
<tr>
<td>Toluene</td>
<td>52.33</td>
<td>62.16</td>
<td>60.24</td>
<td>60.51</td>
</tr>
<tr>
<td>Chloroform</td>
<td>20.75</td>
<td>18.99</td>
<td>38.16</td>
<td>36.49</td>
</tr>
<tr>
<td>Methanol</td>
<td>353.20</td>
<td>282.07</td>
<td>423.68</td>
<td>409.87</td>
</tr>
</tbody>
</table>
Unlike **Chapter 4**, the $Ra^2$ value trends are different and appear to depend on the addition of polystyrene to the base layer. Acetone and toluene have similar $Ra^2$ values. Interestingly, in systems where the PS volume fraction is larger than the PGMA volume fraction, the value for $Ra^2$ for toluene is greater than that of acetone. This can explain that toluene shows greater affinity towards PS, whereas acetone has a preferred affinity to the base layer (as **Chapter 4** revealed as well). Chloroform has the lowest values of $Ra^2$ compared to all solvents for all polymer systems. This means that for all systems, chloroform has the highest affinity to the systems. On the other hand, methanol has the largest (by a factor of ten) value of $Ra^2$, which implies it shows no affinity to the polymeric system components.

The swelling extent was measured for 50 nm thick films of PGMA and of PMMA-co-PGMA that were functionalized with 70 nm of PS and individually exposed to: acetone, toluene, chloroform, and methanol. Three samples were measured for each solvent. **Figure 4. 2** shows the swelling behavior of PGMA-PS and PMMA-co-PGMA-PS functionalized EPLs when exposed to individual analytes. The swelling ratio is determined from **Equation 4. 8**. Because PMMA and PGMA have very similar molecular structures, it was shown in **Chapter 4** that swelling values due to the backbone of the EPLs have similar interaction trends. In other words, comparing these results with **Chapter 4** PGMA swelling (**Figure 4. 2a**) and PMMA-co-PGMA swelling (**Figure 4. 2b**), the response to toluene is much larger when the EPLs are functionalized with PS. Although the $Ra^2$ values for acetone and toluene are similar, toluene seems to swell the films more than acetone. This can be explained, similarly to **Chapter 4**, by the fact that
tethered chains to a substrate have a different structure than when modeled free in solution. Consequently, toluene perhaps is able to reach the PS molecules in the system easier than predicted and swell the system more than predicted by $Ra^2$ estimates.

The Hansen solubility parameters for the PGMA-EA and PMMA-co-PGMA-EA systems are presented in Table 5.5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thin PGMA+EA</th>
<th>Thick PGMA+EA</th>
<th>Thin Copolymer+EA</th>
<th>Thick Copolymer+EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_D, \text{Tot}$</td>
<td>16.54</td>
<td>16.55</td>
<td>16.55</td>
<td>16.54</td>
</tr>
<tr>
<td>$\delta_P, \text{Tot}$</td>
<td>8.17</td>
<td>8.42</td>
<td>8.33</td>
<td>8.19</td>
</tr>
<tr>
<td>$\delta_H, \text{Tot}$</td>
<td>10.07</td>
<td>10.45</td>
<td>10.31</td>
<td>10.10</td>
</tr>
</tbody>
</table>
Figure 5.6. (a) PGMA-PS functionalized EPL and (b) PMMA-co-PGMA-PS functionalized EPL responses to individual analytes.
The $Ra^2$ value for PGMA-EA and PMMA-co-PGMA-EA systems was calculated.

Table 5.4. Calculated estimate $Ra^2$ value for two-component systems of PGMA-EA and PMMA-co-PGMA-EA of different thicknesses. “Thin” corresponds to a base layer thickness of 50nm and “thick” corresponds to a base layer thickness of 100nm.

<table>
<thead>
<tr>
<th></th>
<th>Thin PGMA+EA</th>
<th>Thick PGMA+EA</th>
<th>Thin Copolymer+EA</th>
<th>Thick Copolymer+EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>18.67</td>
<td>20.22</td>
<td>19.62</td>
<td>18.79</td>
</tr>
<tr>
<td>Toluene</td>
<td>119.52</td>
<td>128.99</td>
<td>125.56</td>
<td>120.30</td>
</tr>
<tr>
<td>Chloroform</td>
<td>51.19</td>
<td>57.05</td>
<td>54.91</td>
<td>51.66</td>
</tr>
<tr>
<td>Methanol</td>
<td>174.91</td>
<td>164.02</td>
<td>167.86</td>
<td>173.99</td>
</tr>
</tbody>
</table>

Once again, unlike Chapter 4, the $Ra^2$ value trends are different and appear to depend on the addition of ethanol amine to the base layer. Contrary to systems containing PS, toluene and methanol have similar $Ra^2$ values, which are tenfold higher than those of acetone and chloroform. In the case of EA systems, acetone, instead of chloroform, has the lowest values of $Ra^2$ compared to all solvents for all polymer systems. This means that for all systems, acetone should show the best affinity to the systems.

5.3.3 Foaming of EPLs

From the preliminary studies in Section 5.3.1 the functionalities of choice were narrowed down to carboxy-terminated polystyrene (PS-COOH) (MW: 2,400 g/mol, PDI: 1.12) and ethanol amine (EA). The carboxy end functionality of the PS and the amine functionality of EA allowed for reaction with the epoxy groups present in the PGMA.

5.3.3.1 Foaming of EPLs functionalized with carboxy-terminated polystyrene

Thin PGMA-PS systems foamed 20.9±5.6% versus thicker PGMA-PS films which only foamed 18.1±1.8%. For the thin and thick copolymer-PS systems, a larger extent of foaming was achieved of 31.1±1.9% and 23.6±1.8%, respectively.
Images in Figure 5.7 show the morphological response of the thicker systems when foamed and collapse, revealing shape memory properties. In fact, it can be seen that the morphology and the uniformity of the before foaming and after collapsing is very similar. This implies that the system remembers its original structure due to the fact it relaxes to the same state when exposed to the original environment.

5.3.3.2 Foaming of EPLs functionalized with ethanol amine

The ethanol amine systems foamed much less than for the systems with PS. Thin and thick PGMA films had 3.9±0.5 nm and 11±1.5 nm of grafted EA, respectively. Thin and thick copolymer films had 5.1±0.5 nm and 7.7±1.7 nm of grafted EA, respectively.
Images in Figure 5. 8 show the morphological response of the thicker systems when foamed and collapse, revealing shape memory properties.

![Images of PGMA-EA and PMMA-co-PGMA-EA foams](images)

**Figure 5. 8.** Morphology of PGMA-EA, and PMMA-co-PGMA-EA foams showing shape memory characteristics when exposed to the same initial environment. All images are 1x1 µm, with a height of 30nm

Similarly to the response with PS functionalization, the system shows a return in its morphological structure as before foaming. The ethanol amine systems foamed much less than for the systems with PS. In fact, it is possible to calculate the distance between grafting sites for PS and EA using **Equation 5.2.**

\[
\text{Distance between grafting site} = \frac{4}{(\text{Grafted Chain Density} \times \pi)^{0.5}} \tag{Eq. 5.2}
\]

The distance between grafting sites for 1 nm of PS was calculated to be 2.1 nm, whereas for 1 nm of EA it is 0.35 nm. This implies that for 1 nm, there are 0.47 chains of PS versus 2.9 of EA. This implies that the EA can diffuse into the base layer easily and react...
with the epoxy groups to a much larger extent (higher cross-linking) than PS can. A higher degree of cross-linking prevents the chains to expand to their maximum extent which decreases the foamability of the system. This explains why ethanol amine systems swell to a much lower extent than PS systems.

5.3.4 Response to Analytes

The interaction of the foamed polymer systems with saturated vapor of solvents of different nature was studied, based on the results presented in Figure 5. 6a and Figure 5. 6b. Swelling was performed on the foamed samples to compare swelling extents before and after foaming. Figure 5. 9 reveals that even after foaming, the PGMA and PMMA-co-PGMA functionalized with PS respond to the analytes with the same trends. Interestingly enough, all foamed samples swell more after foaming than before foaming. This can be explained that the vapor analyte can penetrate (diffuse) easier through a foamed network (more free volume) compared to a collapsed layer (before foaming). In other words, after foaming, samples swell to a larger extent than before foaming due to added surface area.

Figure 5. 10 compares the sequential response (unlike Chapter 4 where it was an individual response) to the analytes of a foamed polymer layer modified with carboxy-terminated polystyrene.
Figure 5.9. (a) PGMA-PS functionalized EPL and (b) PMMA-co-PGMA-PS functionalized EPL response to individual analytes comparison before and after foaming.
Figure 5.10. Sequential response to analytes of an base layer modified with carboxy-terminated polystyrene.
It is noticeable that the PMMA-co-PGMA functionalized layer foams to a much larger extent than PGMA-PS systems. This is due to the fact that the PGMA-PS system has a higher cross-linking density compared to PMMA-co-PGMA-PS system.

Acetone seems to have a stronger response than any other analyte. A possible explanation is that, when the system is foamed, stress is induced in the polymer chains. Kinetically trapped in that shape and thermodynamically unstable, the polymer chains relax at the first opportunity. Consequently, acetone has a much stronger response than all the other analytes comparatively, although the $Ra^2$ is slightly higher for acetone than it is for chloroform. It is also clear that the shape memory nanofoam can differentiate between chloroform vapor and its initial environment of liquid chloroform. Generally, it appears that the copolymer-base systems have a much stronger response (collapse) to the analytes. This could be due to the lower cross-linking density present in the system that allow for larger possibility of interaction even with a non-solvent, such as ethanol.

**Figure 5.11** compares the sequential response to the analytes of a foamed polymer layer modified with ethanol amine. As for the PS-COOH modified systems, PMMA-co-PGMA functionalized layer foams to a much larger extent than modified PGMA systems. Once again, this could be due to the higher cross-linking density in the modified PGMA systems.
Figure 5.11. Sequential response to analytes of a base layer modified with ethanolamine.
Comparing layers modified with PS (Figure 5. 10) and layers with EA (Figure 5. 11), the foaming extent is much lower for EA systems. Ethanol Amine is a small molecule that can easily penetrate in the base layer and cross-link it to a higher degree. Consequently, the network does not foam as much as the PS-COOH modified systems. For similar reasons, acetone has a stronger response with EA systems than PS-COOH systems, as it relieves a larger amount of stress. Finally, each functionality causes the systemes to respond differently to each analyte.

5.3.5 Refractive Index Calculations

Reflectometry was implemented to monitor the change in thickness of the systems modified with polystyrene and ethanol amine. The refractive index was calculated on the copolymer systems like for PGMA. Figure 5. 12a-d represents the changes in refractive index (λ=651nm) as a function of normalized change in thickness for the base layers modified with and PS (Figure 5. 12a-b), and base layer modified with EA for both the weighted average and the Bruggeman model. Figure 5. 12 reveals that both models of refractive index give very similar values for refractive index for all systems. In all systems with PMMA-co-PGMA as the base layer, the change in refractive index as a function of change in thickness is much larger than for PGMA systems. This leads to the conclusion that PMMA-co-PGMA systems are much more sensitive to the environment and that it is possible to detect changes in refractive index for any system, which is important for the waveguide resonators detection platform. In addition, the change in refractive index for the ethanol amine systems is much smaller than the systems modified with PS-COOH.
Figure 5.12. Change in Refractive index calculated by weighted average and Bruggeman model as a function of nanofoam thickness change for (a) PGMA-PS, (b) PMMA-co-PGMA-PS, (c) PGMA-EA, and (d) PMMA-co-PGMA-EA.
Once again, this could be due to the fact that systems with EA are much more cross-linked and consequently not as responsive as PS-COOH systems. Nonetheless, the different affinities of each functionality to each analyte allow a specific and selective response.

5.3.6 Waveguide Race Track Resonators

The chemically functionalized nanofoams are placed on wave-guide racetrack resonators that measure the change in propagation of light upon collapsing of the foam as an analyte is being sensed. Consequently, it is of importance to understand if the extent of response the foams is significant to be able to detect a change in refractive index, which was calculated as explained in Section 5.3. The fabricated resonator devices have the same thickness and parameters as described in Section 4.5.

Figure 5.13a-b shows the nanofoams on the resonators when exposed to different analytes and their response. The PGMA-PS systems tested show very particular and distinct responses. Interestingly enough, not all systems show a shift towards higher wavelengths upon exposure to analytes. As a reminder, a shift towards higher wavelengths corresponds to an increase in refractive index, which is what is expected as the foams partially collapse. Again, this can be hypothesized by the fact that pores, upon collapse coalesce into larger pore, allowing for larger wavelengths to travel through.\(^8\)

The fact that the PMMA-co-PGMA-PS shows a different trend than PGMA-PS signifies that there is a different mechanism upon collapsing that occurs when the chains relax. It is hypothesized that as the chemically modified nanofoams collapse, the pores in
Figure 5.13. Optical response of micro disk resonators covered with nanofoams layers post-exposure to different analytes. (A) PGMA-PS nanofoam (B) PMMA-co-PGMA-PS nanofoam.
the copolymer merge. Nonetheless, the resonators showed that the detection platform was successful even for chemically functionalized nanofoams.

5.4 Conclusions

The fabrication of functionalized shape memory polymer nanofoams was successful with both PS-COOH and EA, given the versatile chemistry that the PGMA epoxy groups offer. Chemistries penetrate the structure allowing for chemical modification within the entire base layer, allowing for an efficient response. The copolymer seemed to be able to be functionalized to a larger extent (more PS and more EA was grafted) due to its ability to swell more, once again due to a lower amount of cross-linking agents. For the same reasons, EA systems for both PGMA and PMMA-co-PGMA foamed less than the PS systems. The chemically functionalized shape memory nanofoams reveal shape memory behavior due to the fact that, when exposed to their original environment, they collapsed and returned to their original thickness.

Each analyte acts as a plasticizer causing a localized response (partial collapse) where the functionality is present. Calculations of the change in refractive index before and after each exposure to the analytes prove that the response mechanism is effective. In all systems with PMMA-co-PGMA as the base layer, the change in refractive index as a function of change in thickness is much larger than for PGMA systems. Consequently, PMMA-co-PGMA systems seem more sensitive to the environment, revealing the possibility to detect changes in refractive index for any system.
Finally, it was shown that the waveguide racetrack resonators prove to be a feasible platform for chemically functionalized shape memory nanofoams for unattended sensing. Specifically, the PGMA-PS systems tested show very distinct and unique responses. Not all systems show a shift towards higher wavelengths upon exposure to analytes. In addition, PMMA-co-PGMA-PS shows a different trend than PGMA-PS. The resonators showed that the detection platform was successful for chemically functionalized nanofoams.

Chapter 5 shows the successful synthesis of chemically functionalized shape memory nanofoams. It is possible to tailor the properties of the films such that each chemical functionality shows selectivity and specificity to target analyte. Chapter 5 reveals the chemically functionalized EPLs provide a much more efficient response than just simple EPLs.

5.5 References


6 GRADIENT SHAPE MEMORY NANOFOAMS

6.1 Introduction

In Chapter 5 it was shown that successful chemical modification of the base layers was achieved. It was determined that adding chemical functionalities to PGMA and PMMA-co-PGMA altered the response to the analytes. However, to detect an analyte response from several different analytes, individually modified foam films are needed. To be able to detect an analyte using just one nanofoam film, multiple chemical functionalities need to be present on the same layer at the same time. Ideally, different concentrations of each chemically functionality should be present across the entire base layer; this would allow each single moiety to respond in a unique and singular way. To this end, Chapter 6 focuses on the modification of the base layers with gradient chemical functionalities and the gradient layers’ response to various analytes.

Surface chemical gradients have attracted considerable attention for applications that involve biomolecular interactions, chemical affinity, nanotribology, and microfluidics. Different techniques to create gradients on various substrates have been implemented. The most widely used methods to create surface gradients include templates, lithography, and temperature differences. To the best of our knowledge, no work has been done on nanofoam gradients for sensing applications. In addition, the chemical gradients proposed in literature are generally on the surface of the substrate/material, and not within a structure. [1] Finally, no work has been shown, to the
best of our knowledge, to incorporate functionalities in a gradient like manner in shape memory materials.

Chapter 6 first reports a one-dimensional (1D) one-component nanofoam gradient synthesis. Then, a secondary method of producing a 1D two-component system will be shown to impart much larger specificity due to the added chemical composition variety. In addition, it is shown that the added chemical functionalities impart specificity and selectivity of the system with the potential of being used as unattended sensors on waveguide resonators.

6.2 Experimental

6.2.1 1D one-component gradient

To create a 1D one-component chemical gradient, multiple steps were conducted. Figure 6. 1 shows a schematic of each step. First, the silicon wafer substrate was dip-coated in 2% solution of PS-COOH from chloroform (Figure 6. 1a). The solution also contained 30 w/v% of unreactive high molecular weight polystyrene to prevent dewetting, as described in Chapter 5. The dip-coated layer was chemically grafted for four hours to the PGMA layer using a thermal gradient stage (3x1cm, Chapter 3) to create a temperature gradient across a 30 mm sample. The temperature gradient created along the stage was in the range of 85-175°C along 30 mm distance (Figure 6.1b).

6.2.2 1D two-component gradient

To synthesize 1D two-component gradient, EA from the same solution described in Chapter 5 was anchored to the PGMA/PS gradient film created in Section 6.2.1. To
create a PGMA/PS/EA dual gradient, the PGMA/PS gradient was set in a 2.5% solution of EA in chloroform for 4 hours at 35°C to allow for the amine groups to react with the epoxy groups remaining in the PGMA/PS system. The intention was to obtain a gradient of EA directed in the opposite direction to the PS gradient synthesized previously (Figure 6.1c).

The sample is then foamed as described in Chapter 4.2.3.

**Figure 6.1.** Schematic representation of the production of 1D one-component and two-component chemical gradients which includes dip-coating PS-COOH (a) and placing it on a thermal stage (b) to create a 1D one-component gradient. To create a PGMA/PS/EA dual gradient (c), the PGMA/PS gradient was set in a solution of EA in chloroform with the intention of obtaining a gradient of EA directed in the opposite direction to the PS gradient synthesized previously. The sample is then swollen and freeze dried to create a 1D 2-component system.

### 6.2.3 Characterization and techniques

Both the PS-functionalized 1D one-component systems and the 1D two-component PS/EA functionalized films are treated and characterized in the same manner. The chemically functionalized base layers were exposed to analytes as described in
Section 4.2.4. All the samples were characterized using the techniques discussed in Section 4.2.5. The refractive index change upon exposure to analytes is calculated using Equation 4.1. Statistical analysis is conducted as described in Section 4.2.7.

6.3 Results and Discussion

6.3.1 Synthesis and Characterization of 1D one-component system

A 1D multi component chemical gradient was formed by depositing 85±1 nm thick base layer of PGMA. The versatile chemistry of the epoxy groups present in the PGMA chemical structure offer flexibility in the selection of molecules/macromolecules used to chemically functionalize it in a gradient manner. A PS-COOH layer of 160 nm was deposited on the top of PGMA layer by dip-coating. The samples were placed on the thermal gradient stage and annealed. Because the rate of chemical reaction between carboxy and epoxy group is temperature dependent, different amounts of PS were grafted to the PGMA along the sample corresponding to the temperatures at a particular point on the surface. Figure 6.2 presents the grafted gradient thickness.
The measurements of the amount of PS attached into PGMA in Figure 6.2 revealed that the effective thickness of the PS layer grafted into the PGMA film varied from 3 nm on the cold end of the stage to 91 nm on the hot end of the stage. AFM was used to characterize the change in morphology as a function of temperature (and consequently grafted thickness). Figure 6.3 reveals that the PS layer morphology was uniform and smooth. The results obtained demonstrated that 1D PS/PGMA gradient film was successfully synthesized.

Figure 6.3. AFM topography images of PS/PGMA gradient film. Arrow indicates direction of PS gradient layer from PS-rich to PS-poor side. Image size 1x1 micron, height of 10nm. Results produced by Yuriy Galabura.
Similarly to Chapter 4 and Chapter 5, the $Ra^2$ values were calculated for the different points across the gradients. To find the Hansen solubility parameter components, a simple weighted average formula (Eq. 6.2) was used.

$$\delta_{x,\text{system}} = \mu_{\text{PGMA}} \delta_{x,\text{PGMA}} + \mu_{\text{PS}} \delta_{x,\text{PS}}$$  \hspace{1cm} \text{Eq. 6.1}

where $\delta_x$ is either the polar, dipole-dipole, or hydrogen Hansen component, for the system total, PGMA and PS. The calculated values of each Hansen solubility component for the different positions along the gradient thicknesses in Figure 6.2 above, are calculated using Equation 4.6 and presented in Table 6.1.

<table>
<thead>
<tr>
<th>Geometrical Position, mm</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_p_{\text{system}}$</td>
<td>18.89</td>
<td>18.07</td>
<td>17.23</td>
<td>17.02</td>
<td>16.94</td>
</tr>
<tr>
<td>$\delta_D_{\text{system}}$</td>
<td>6.71</td>
<td>7.01</td>
<td>7.33</td>
<td>7.41</td>
<td>7.44</td>
</tr>
<tr>
<td>$\delta_H_{\text{system}}$</td>
<td>6.77</td>
<td>7.59</td>
<td>8.46</td>
<td>8.67</td>
<td>8.75</td>
</tr>
</tbody>
</table>

From the values in Table 6.1 it is possible to calculate the $Ra^2$ values for each chemical composition along the gradient. The resulting $Ra^2$ values explain the expected affinity between each chemical composition (geometrical position) and the analytes. Table 6.2 shows the calculated $Ra^2$ values as a function of chemical composition.
Similarly to Chapter 4 and Chapter 5, acetone seems to have low values for the interaction parameter, signifying the strongest interaction, specifically after 15 mm, when the amount of grafted PS to PGMA decreases from 80 nm to 15 nm. Again, this can be explained as the fact that Hansen solubility parameters are used to model polymers in solution and not polymer systems grafted to a substrate and cross-linked. Chloroform has the second lowest value for $R_a^2$, signifying that each chemical composition appears to have a strong interaction affinity for it. On the other hand, methanol has the largest calculated $R_a^2$ which explains that methanol experiences the lowest affinity to the compositions. The values for toluene do not follow a general pattern. The calculations show that each chemical composition will collapse uniquely to each analyte due to the imparted specificity and selectivity along the gradient.

| Table 6.2. Calculated $R_a^2$ values to evaluate the interaction between each analyte and each singular chemical composition. |
|---|---|---|---|---|---|
| Geometrical Position, mm | 5 | 10 | 15 | 20 | 25 |
| Acetone | 59.54 | 38.34 | 23.50 | 20.96 | 20.11 |
| Toluene | 53.99 | 62.78 | 79.22 | 84.48 | 86.59 |
| Chloroform | 18.84 | 19.17 | 26.79 | 29.84 | 31.12 |
| Methanol | 329.93 | 279.64 | 234.44 | 224.32 | 220.62 |
6.3.2 Synthesis and Characterization of 1D two-component system

To synthesize 1D two-component gradient a second polymer was grafted to the PS/PGMA gradient film. The intention was to obtain a gradient of EA directed in the opposite direction to the PS gradient synthesized previously, taking advantage of the varied concentration of the epoxy groups along the sample.

To create a 1D two-component system with PGMA/PS/EA, 145±3 nm thick layer of PGMA was deposited on silicon wafers via dip-coating technique. PS-COOH was grafted on the PGMA film using a thermal gradient stage. Figure 6.4 presents the gradient thickness measurements of the 1D two-component system.

The measurements revealed that the thickness of the PS layer grafted into the PGMA film varied from 11±1.2 nm on the cold end of the stage to 17.5±1.3 nm on the hot end of the stage. To synthesize 1D two-component gradient, EA was grafted to the
PGMA/PS gradient film. The intention is to obtain a gradient of EA directed in the opposite direction to the PS gradient synthesized previously. In fact, the thickness of the grafted EA layer was measured and showed a variation from 39.8±2.2 nm to 58.5±2.3 nm in the opposite direction of PS gradient, as shown in Figure 6.4. As for the 1D one-component system, AFM was utilized to characterize the morphology of the 1D two-component system.

AFM revealed that the PS layer and of the subsequent EA layer was uniform, as seen in Figure 6.5. From position 5 to 25, the amount of PS grafted to PGMA increases. The morphology, in fact, changes, although not drastically. This could signify that the majority of the grafting occurs inside the base layer, with no major effect on the surface morphology overall. AFM images also show that the morphology for the EA grafting changes across the geometrical position along the gradient. On the results obtained demonstrated that 1D PGMA/PS/EA gradient film was successfully produced.
Similarly to Chapter 4 and Chapter 5, the $Ra^2$ values were calculated for the different points across the gradients. To find the Hansen solubility parameter components, a simple weighted average formula (Eq. 6.2) was used.

$$\delta_{x,\text{system}} = \mu_{\text{PGMA}} \delta_{x,\text{PGMA}} + \mu_{\text{PS}} \delta_{x,\text{PS}} + \mu_{\text{EA}} \delta_{x,\text{EA}}$$  \hspace{1cm} \text{Eq. 6.2}

where $\delta_i$ is either the polar, dipole-dipole, or hydrogen Hansen component, for the system total, PGMA, PS and EA. The calculated values of each Hansen solubility component for the different positions along the gradient thicknesses in Figure 6.4 above, are calculated using Equation 4.6 and presented in Table 6.2.

**Table 6.2.** Calculated Hansen solubility parameters for the 1D two-component system PGMA/PS/EA as a function of geometrical position.

<table>
<thead>
<tr>
<th>Geometrical Position, mm</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{P,\text{system}}$</td>
<td>7.80</td>
<td>8.61</td>
<td>9.52</td>
<td>9.81</td>
<td>10.25</td>
</tr>
<tr>
<td>$\delta_{H,\text{system}}$</td>
<td>8.56</td>
<td>10.16</td>
<td>11.88</td>
<td>12.39</td>
<td>13.09</td>
</tr>
</tbody>
</table>

From the values in Table 6.2 it is possible to calculate the $Ra^2$ values for each chemical composition along the gradient. The resulting $Ra^2$ values explain the expected affinity between each chemical composition (geometrical position) and the analytes. Table 6.4 shows the calculated $Ra^2$ values as a function of chemical composition.

**Table 6.4.** Calculated $Ra^2$ values to evaluate the interaction between each analyte and each singular chemical composition.

<table>
<thead>
<tr>
<th>Geometrical Position, mm</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>48.92</td>
<td>35.68</td>
<td>35.66</td>
<td>38.52</td>
<td>45.66</td>
</tr>
<tr>
<td>Toluene</td>
<td>85.59</td>
<td>118.73</td>
<td>166.25</td>
<td>182.48</td>
<td>205.68</td>
</tr>
<tr>
<td>Chloroform</td>
<td>33.11</td>
<td>50.33</td>
<td>80.97</td>
<td>92.19</td>
<td>108.58</td>
</tr>
<tr>
<td>Methanol</td>
<td>259.63</td>
<td>191.62</td>
<td>133.46</td>
<td>119.09</td>
<td>102.79</td>
</tr>
</tbody>
</table>
Similarly to Chapter 4 and Chapter 5, acetone seems to have the lowest value for the interaction parameter, signifying the strongest interaction. Again, this can be explained as the fact that Hansen solubility parameters are used to model polymers in solution and not polymer systems grafted to a substrate and cross-linked. Chloroform values of $Ra^2$ increase as the amount of EA increases in the system. This implies that chloroform has a stronger affinity to PS than for EA. On the other hand, values for methanol significantly decrease as the amount of EA increases in the system. Finally, the values for toluene follow a similar pattern to chloroform. Toluene is very selective to PS and consequently values of $Ra^2$ increase with decreasing amount of PS. It is apparent that since each chemical composition is different along the gradient, all the interaction values differ. This lines up with the hypothesis that each chemical composition will collapse uniquely to each analyte due to the imparted specificity and selectivity along the gradient.

6.3.2 Foaming of 1D gradients

6.3.2.1 Foaming of 1D one-component gradient

In order to permanently record chemical interaction events, the material should have shape memory properties. Increment in thickness of PS/PGMA film as a result of the foaming was on the level of 15% according to the ellipsometric measurements (Figure 6.6). Figure 6.6 reveals the total foamed thickness was not flat but varied 100 nm over 3 cm.
The change in morphology of the PS/PGMA gradients after foaming was monitored by AFM. **Figure 6.7** demonstrates changes in structure of the film and development of pores on submicro- and nano-levels.

6.3.2.2 **Foaming of 1D two-component gradient**

Reflectometry was used to determine the change in thickness of the polymer gradient films after foaming. Increment in thickness of PGMA/PS/EA gradient as a
result of foaming was on the level of 8.5±1.9 % according to the reflectometry measurements (Figure 6.8).

![Figure 6.8](image.png)

**Figure 6.8.** Reflectometry measurements of foamed 1D two-component gradient as a function geometric position.

From data in Figure 6.8 it is possible to note that the amount of foaming increases moving from the PS-poor side to the PS-rich side. It can be hypothesized that the EA, being a small molecule, cross-links much more epoxy groups, which are more readily available for reaction in the PS-poor side. As the amount of available epoxy groups decreases (moving towards the PS-rich side), less EA gets grafted, causing the system to be less cross-linked and hence capable of foaming more. This dynamic is advantageous as ultimately it was possible to achieve a flat foamed surface across the entire geometry.
of the sample, with an average foamed thickness of 225±3.6 nm. This is necessary for an
effective unattended sensor to efficiently monitor the response to environmental changes.

The change in morphology of PGMA/PS/EA gradients after foaming was monitored by AFM.

![AFM topographical images](image)

**Figure 6.9** AFM topographical images of before (upper row) and after foaming (second row) as a functional of geometrical position across the sample, with clear evidence of localized changes in structure. The images are 1x1µm; height: 35nm. The numbers on the top of the figure represent the geometrical position (in mm) across the gradient.

**Figure 6.9** images demonstrated changes in structure of the film and development of the pores on submicro- and nano- levels. It appears that the side with less EA and more PS grafted (Spot 25 in **Figure 6.9**) had a larger extent of porosity than the side with more EA (Spot 5 in **Figure 6.9**). This can be explained by the lower level of cross-linking on Spot 25 compared to Spot 5. In fact, it was shown in Chapter 5 that due to the fact that ethanol amine is a smaller molecule compared to PS-COOH, the level of cross-linking where EA is present is much larger. Higher cross-linking density results in lower mobility of the chains and consequently a lower level of foaming and porosity formation upon foaming.
6.3.3 Response to Analytes

6.3.3.1 Response to analytes of 1D one-component system

To understand the 1D one-component foam response to analytes, it was exposed to various solvents in a sequential manner, to understand the degree of response each component is responsible for. The interaction of the foamed gradients was with saturated vapor of methanol and chloroform vapor. Specifically, the gradient nanofoam was first exposed to saturated vapor of methanol and then, after drying and characterization, it was exposed to the saturated vapor of chloroform. The changes in an effective thickness were monitored by ellipsometry after every exposition to the solvent vapor. The ellipsometric measurements revealed a gradual decrease in thickness of the PS/PGMA gradient after the sequential interaction with methanol and chloroform saturated vapors respectively (Figure 6.10).

![Figure 6.10. Variation of the thickness of the PS/PGMA gradient foam after sequential exposing to methanol and chloroform versus position on the sample. Results produced by Yuriy Galabura.](image-url)
AFM was used to characterize the change in morphology. AFM images (Figure 6. 11) demonstrated gradual change in morphology of the surface and decrease in RMS roughness from 5.2 nm for the surface of foamed gradient to 2.5 nm after exposing the sample to saturated methanol vapor and down to 1 nm after sequential exposing of the sample to the saturated chloroform vapor.

![Figure 6. 11. AFM images of the PS/PGMA gradient film. From left to right: AFM images of the PS/PGMA gradient before foaming, after foaming, after exposing sample to the methanol vapor, and after exposing sample to the chloroform vapor. Size 1x1 um, height 20nm. Results produced by Yuriy Galabura.](Image)

It is imperative to understand the individual behavior of the PS/PGMA to different analytes rather than the response in sequential order. The obtained results clearly indicated that the extent of the foam collapsing at different places of the gradient is determined by the thermodynamic quality of the solvent. So, each PS/PGMA gradient showed unique collapsing behavior (“fingerprint”) as a function of the type of solvent vapor.

6.3.3.2 Response to analytes of 1D two-component system

To understand if the 1D two-component foam is responsive system, various analytes were tested in a sequential manner, to understand the degree of response each component is responsible for. In Figure 6. 12, the thickness response to acetone, toluene, and chloroform vapor is shown as a function of geometrical position.
The obtained results clearly indicate that the extent of the foam collapsing at different places of the gradient is determined by the thermodynamic quality of the solvent (Table 6.2). So, each geometrical position showed unique collapsing behavior ("fingerprint") as a function of the type of solvent vapor. This implies that the chemical composition determines the level of specificity and sensitivity of the system.

Acetone is a good solvent for all chemical composition, according to results in Table 6.2. Consequently, the collapse profile due to acetone represents the behavior of the PGMA/PS/EA components as they interact with that analyte. In addition, acetone has a moderate affinity to polystyrene. Consequently, the percent response to acetone is higher in the PS-rich region. Toluene is highly selective to PS. The profile in Figure 6.12 represents the response due (mostly) to the PS component. To keep in mind, since the exposure of solvents was done in sequential order (acetone first, then toluene), the profile seen is unique to this system as it is highly dependent on the exposure to acetone. Consequently, it is not possible to conclude that the PS-rich region should have shown a larger collapse as the system had already gone major changes with acetone. This is advantageous for unattended sensing as the system has a unique response (that can be measured) that is not predictable. Chloroform in saturated vapor was the third analyte to be exposed to the 1D two-component system. Once again the profile is unique to the system and dependent on the first two response profiles. Important to notice is that chloroform vapor did not cause the foam to fully collapse and return to its original position at any point across the gradient. This means that the system can differentiate between similar environments.
Figure 6.12. 1D two-component foam PGMA/PS/EA response to various analytes in a sequential manner, to understand the degree of response each component is responsible for.
**Figure 6. 12** reveals two critical things. The first conclusion is that each specific point across the gradient shows a different response from all other points for each analyte. This result implies that the diverse chemical composition at each point imparts selectivity in the system. The second conclusion is that each analyte causes the system to collapse creating a unique thickness pattern targeted to the specific chemical, imparting specificity to the system.

It should be noted that, due to the fact the system is cross-linked, there are residual stresses in the nanofoam system. These stresses are partially relieved when the analyte, which acts as a plasticizer, is present in the environment. Consequently, it is hypothesized that as one location collapses in the presence of a specific analyte, it can cause the rest of the inter-linked network (which is in a temporary more relaxed state due to plasticization effects) to shift and alter its morphology and thickness. This physical change could also be a reason behind the change in profile of the gradient.

AFM images also revealed change in morphology before and after exposing of the PGMAPS/ETA gradients to the vapors, as shown in **Figure 6.13**.
The change in morphology upon subsequent exposures of different environments is clearly observed. Of course, it is important to notice that upon exposure to its original environment (liquid chloroform), the morphology completely goes back to its original state. Consequently, it can be concluded that a successful 1D two-component system gradient shape memory material was produced.

Statistical analysis (Chapter 4.2.6) was used to analyze the significance in change in thickness due to the exposure to the different analytes. In other words, the results reveal if the thickness profile obtained by acetone is significantly different than that of toluene. The change in profile of toluene versus vapor chloroform was also
analyzed, as well as comparing vapor and liquid chloroform responses. The results are shown in Table 6.3.

**Table 6.3. Statistical Significance in Variance Between Analytes.**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Position, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Acetone - Toluene</td>
<td>1.17</td>
</tr>
<tr>
<td>Toluene - Chloroform V</td>
<td>0.23</td>
</tr>
<tr>
<td>Chloroform (V)- (L)</td>
<td>3.71</td>
</tr>
</tbody>
</table>

Statistical analysis reveals that there is a significant difference in the variance between acetone and toluene and between toluene and vapor chloroform, confirming that the system really has specificity. Statistical analysis did not show a significant variance in the profiles resulting from vapor and liquid chloroform.

Statistical analysis was also performed to understand if there is, in effect, a selectivity of the system imparted by the chemical composition. To do so, the F-test was performed comparing the response obtained at each point along the gradient for each analyte. The results are shown in Table 6.4.

**Table 6.4. Statistical Significance in Variance Between Each Point.**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Position, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-10</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.85</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.00</td>
</tr>
<tr>
<td>Chloroform (V)</td>
<td>0.23</td>
</tr>
<tr>
<td>Chloroform (L)</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The results reveal that the change in thickness between each point for each analyte has a statistical significance. Consequently it is possible to say with 95% confidence that there is a statistical significance and that the system shows selectivity to the analytes.
6.3.4 Refractive Index Calculation

The refractive index was calculated as described in Chapter 4.2.6. The modeling results are shown in Figure 6.14. The results show that the effective change in refractive index at each point across the gradient is unique to the response to a specific analyte. The change in refractive index is large enough to affect the local optical properties such as optical absorption. In addition, Figure 6.14 shows that upon collapsing the refractive index goes back to the original value for each point. The extent of response shows that it is possible to detect and identify the analyte as a function of geometric position by changes in the optical properties.
Figure 6.14. Calculated refractive index of 1D two-component system showing the effective change in refractive index at each point across the gradient as a unique response to a specific analyte.
6.4 Conclusions

Chapter 6 discusses the synthesis and characterization of a 1D one- and two-component system with PGMA/PS and PGMA/PS/EA. The results obtained demonstrated that 1D one-component and two-component gradient films was successfully produced.

The 1D one and two component systems proved to have shape memory property. According to ellipsometry, the 1D one-component systems foamed up to 15%. The 1D two-component systems foamed up to 9%. AFM images demonstrated changes in structure of the films for both systems. It was noticeable that the amount of foaming increases moving from the PS-poor side to the PS-rich side. In addition, it was possible to achieve a flat foamed surface across the entire geometry of the sample. The results indicated that the extent of the foam collapse at different places of the gradient is determined by the thermodynamic quality of the solvent. Consequently, it can be said that each geometrical position showed unique fingerprint for each solvent type.

Statistical analysis revealed that, within 95% confidence, there is a significant difference in the variance between acetone and toluene and between toluene and vapor chloroform, confirming that the system has specificity. Statistical analysis did not show a significant variance in the profiles resulting from vapor and liquid chloroform.

The response to various analytes was studied as an independent interaction, and not sequential. The results clearly indicate that the extent of the foam collapsing at different places of the gradients is determined by the thermodynamic quality of the solvent. Similarly to a 1D two-component gradient, each geometrical position showed a
very unique collapsing behavior as a function of the solvent type. This implies that the chemical composition determines the level of specificity and sensitivity of the system.

Finally, Chapter 6 concludes that successful 1D one- and two-component system gradient shape memory nanofoams were produced, with high specificity and selectivity. In addition, the extent of response reveals that it is possible to detect and identify the analyte as a function of chemical composition.

### 6.5 References

7 ORTHOGONAL GRADIENTS ON SHAPE MEMORY
NANOFOAMS

7.1 Introduction

In Chapter 6 it was shown that chemical modification in a gradient manner of base layers can be achieved. It was determined that adding chemical functionalities whose concentrations varied 180 degrees from each other to PGMA and PMMA-co-PGMA altered the response to the analytes. This response mechanism showed that varying the concentration of a chemical functionality in one specific direction increases the selectivity and specificity of the system. Results obtained in Chapter 6 leads to believe that the efficiency of the response could be further improved if each position across the entire gradient had a unique chemical composition. To this end, Chapter 7 focuses on creating chemical gradients that are orthogonal to each other with the purpose of creating a nanofoam film with unique chemical compositions at each point. To the best of our knowledge, no previous work has been done to create orthogonal chemical gradients on shape memory nanofoams to enhance the detection of multiple analytes and retain memory of the exposure for unattended sensing purposes.

Chapter 7 has the purpose of providing different ways to approach the synthesis and characterization of chemical gradients shape memory nanofoams. It will report on how a 2D one-component gradient is synthesized and foamed to have shape memory properties. Then, a simple secondary method of producing a 2D two-component system will be described which imparts much larger specificity due to the added chemical composition variety. Finally, the 2D two-component system with an orthogonal gradient
chemical composition is shown to be selective and specific when exposed to different environments. In addition, it has imparted memory of the exposure to the various environments and has the potential to be used as an element for an unattended sensor.

7.2 Experimental

To produce 2D two-component orthogonal gradient, a thermal stage was designed (Chapter 3) and fabricated at the Machine Shop on Clemson University campus (Figure 7.1).

![Figure 7.1](image.png)

Figure 7.1. Actual aluminum stage with larger diameter holes (0.25") for heating and cooling, smaller holes (0.027") for thermocouples to control temperature over 1 inch gradient (left to right in image). Stage made of aluminum, insulated with Teflon. Full stage size is 3.5"x1.5". Usual sample size, 1"x1".

Aluminum was used as the heat transfer medium and Teflon as the insulating agent. The cartridge heater is controlled by a PI controller (Omega Engineering Inc.). The heat sinks consist of water running directly through holes in the aluminum block. The water temperature is controlled using a circulating bath (VWR). A 60° temperature gradient can be achieved over one inch using the stage.
To create an orthogonal one-component gradient, a 1x1 in clean silicon wafer is dip coated using a 2% solution of PGMA in chloroform. Once the PGMA layer is annealed and rinsed, it is then dip-coated in a 2% solution of PS-COOH in chloroform. The sample is then placed on the aluminum stage for 2 hours with the heater equilibrated to 140°C, and the water heat sinks set at 65°C. These set points produced an actual temperature gradient that varied linearly from 150°C-91°C. The sample is then rinsed in chloroform 3 times for 30 min, with replacement of solvent every 30 min.

To produce a two-component orthogonal gradient, the one-component gradient sample described above is rinsed and let dry at ambient conditions. The sample is then dip coated in a 2% solution from chloroform of PVP-OH. The sample is then rotated 90° degrees (respective to the original PS-COOH gradient positioning) and placed on the aluminum stage for 2 hours with the heater equilibrated to 150°C, and the water heat sinks set at 75°C. These set points produced an actual temperature gradient that varied linearly from 140°C-82°C. The sample is then rinsed in chloroform 3 times for 30 min, with replacement of solvent every 30 min. The sample is then foamed as described in Section 4.2.3.

7.3 Results and Discussion

7.3.1 Synthesis and Characterization of 2D chemical gradient system

To create a 2D system with PGMA/PS/PVP, 101±25.3 nm thick layer of PGMA was deposited on silicon wafers via the dip-coating technique. PS-COOH layer was deposited on the PGMA films and the polymer was grafted for 2 hours using the thermal
gradient stage with an actual temperature gradient of 150°C on the hot end and cold end of 91°C. A second polymer, hydroxyl terminated PVP was grafted to the PS/PGMA gradient film. The intention was to obtain a gradient of PVP directed 90° clockwise in direction to the PS gradient synthesized previously, taking advantage of the varied concentration of the epoxy groups along the sample. The PV-OH gradient was produced using a temperature gradient of hot to cold of 140-82°C for 2 hours. The temperature gradient was different to compensate for the different glass transition temperature \(T_g\) of the PS and PVP. In fact, the \(T_g\) of PVP-OH is 66°C and the \(T_g\) for PS-COOH is 79°C (as reported by Polymer Source, Inc.) This 90° change created a 2D two-component orthogonal system with a very specific and unique composition at each point across the gradient.

Figure 7. 2a-e shows the gradients at each selected profile along the PS gradient (average of six samples). It reveals that, anywhere along the sample, the chemical composition ratio between PGMA, PS, and PVP is unique. Across the entire sample, the PS gradient is uniform from the hot end (spot 1) to the cold end (spot 5) (Figure 7. 2a through Figure 7. 2e). On average, the PS gradient achieved over one inch was of 107.7±4.1 nm on the hot end and 71.24±2.24 nm for the cold end. On the other hand, the gradient for PVP changed radially across the sample, which is why the composition at each location is unique. For example, it is noticeable that the PVP rich region (Figure 7. 2a, spot 5) has double the PVP grafted that Figure 7. 2e, spot 5. Consequently, the PVP gradients varied from 60 nm over the size of the sample (1 inch) in the PVP rich end, to about 30 nm on the cold end.
Figure 7.2. 2D two-component gradients corresponding to grafted PS on PGMA and grafted PVP on PGMA/PS, showing the gradients across various positions along the samples, including the respecting PS to PVP ratio.
The morphology was also monitored with AFM. Figure 7.3 shows that at each location across the gradient, the morphology is different, revealing the different chemical compositions. It is noticeable that the morphology decreases in roughness as the amount of grafting decreases from spot 1 (high PS, high PVP) to spot 4 (low PVP, low PS) (Figure 7.3).

![Figure 7.3. Morphology differences at the different composition locations across the samples.](image)

### 7.3.2 Hansen solubility parameter calculation for 2D chemical gradient systems

Similarly to previous chapters, the Hansen solubility parameters for the PGMA-PS gradient films and for the PGMA-PS-PVP orthogonal gradient films were calculated using a simple weighted average approach (Eq. 7.1 and Eq. 7.2b).

\[
\delta_{\text{system}} = \mu_{\text{PGMA}} \delta_{\text{x,PGMA}} + \mu_{\text{PS}} \delta_{\text{x,PS}} \quad \text{Eq. 7.1a}
\]

\[
\delta_{\text{system}} = \mu_{\text{PGMA}} \delta_{\text{x,PGMA}} + \mu_{\text{PS}} \delta_{\text{x,PS}} + \mu_{\text{PVP}} \delta_{\text{x,PVP}} \quad \text{Eq. 7.2b}
\]

where \(\delta_\alpha\) is either the polar, dipole-dipole, or hydrogen Hansen component, for the system total, PGMA, PS, and PVP.
7.3.2.1 Hansen solubility parameter calculation for PGMA-PS gradient

The calculated values of each Hansen solubility component for the different positions along the gradient films in Figure 7. 2a-e above, are calculated using Eq. 4. 6 and presented in Table 7. 1a-c. In Table 7. 1a-c and from here on forward, each location across the gradient will be referred to as a x,y coordinate systems, Position x,y, where x is any value between 1-5 that represent the row (PS gradient hot to cold) and y is any value from 1-5 representing the column. The distance between each position is 3 mm. Position 1 represents the hot end of the gradient (where more of that functionality is present) and position 5 represents the colder end of the gradient (where less functionality is present).

It can be seen that each Hansen solubility component varies as a function of the chemical composition across the PS gradient. The calculated $Ra^2$ values for each position along the gradient and its affinity with each analyte is presented Figure 7. 4a-d. Similarly to previous discussions in the results section of the other chapters, it can be seen that the range of $Ra^2$ values changes almost tenfold, going from a good solvent, like chloroform, to a bad solvent, like methanol. Unlike the results discussed in other chapters though, in the case of a PS gradient, it can be seen that each $Ra^2$ value varies linearly in the direction of the gradient.
Table 7.1a. Dipole Component Hansen Solubility Parameter for PGMA-PS gradient.

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Table 7.1b. Polar Component Hansen Solubility Parameter for PGMA-PS gradient.

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Table 7.1c. Hydrogen Component Hansen Solubility Parameter for PGMA-PS gradient.

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Figure 7.4. PGMA-PS $R^2$ value as a function of geometrical position along the PS gradient for (a) Acetone, (b) toluene, (c) chloroform, and (d) methanol.
The direction of the variation depends on the affinity of the PGMA-PS composition to the analyte. For acetone in Figure 7. 4a appears that where there is more PS (position1), the $Ra^2$ values are larger, indicating that PS has a lower affinity to acetone than PGMA (since at position 5, where there is little PS, there is more of the PGMA functionality). On the other hand, the $Ra^2$ values for toluene in Figure 7. 4b reveal the opposite trend. In fact, it shows that where there is more PS present, the values for $Ra^2$ are lower, signifying that PS has a much stronger affinity to toluene than PGMA does. Chloroform has a similar trend to acetone as expected from previous results in other chapters. Acetone and chloroform had very similar responses. Finally, the $Ra^2$ values for methanol. Figure 7. 4d) also vary in the same direction as for acetone and chloroform. The main difference in the case of methanol is that the values of $Ra^2$ are ten times larger than for any other solvents. Although that implies that overall methanol has poor affinity to both PGMA or PS functionality, it appears to prefer PGMA.

7.3.2.2 Hansen solubility parameter calculation for PGMA-PS-PVP gradient

The calculated values of each Hansen solubility component for the different positions along the PGMA-PS-PVP gradient thicknesses in Figure 7. 2a-e above, are calculated using Eq. 4.6 and presented in Table 7.2a-c. In Table 7.2a-c and from here on forward, each location across the gradient will be referred to as a $x,y$ coordinate systems, Position $x,y$, where $x$ is any value between 1-5 that represent the row (PS gradient hot to cold) and $y$ is any value from 1-5 representing the PVP gradient (hot to cold). Positions 1 represent the hot end of the gradients (where more of that functionality is present) and positions 5 represent the colder end of the gradient (where less functionality is present).
It can be seen that each Hansen solubility component varies as a function of the chemical composition across the PS and PVP gradients. In addition, all the components have different values than for the PS gradient only. Specifically, a large difference is noticeable for the hydrogen component of the Hansen solubility parameter, due to the polarity of the PVP functionality. The calculated $Ra^2$ values for each position along the gradients and their affinity with each analyte are presented in Figure 7.5a-d.

Similarly to previous discussions, the range of $Ra^2$ values changes almost tenfold, going from a good solvent, like chloroform, to a bad solvent, such as methanol. Differently than results reported in other chapters though, in the case of a PS-PVP 2D gradient, it can be seen that each $Ra^2$ value varies radially, independent of the directions of the gradients. The directions of the variation depend on the affinity of the chemical composition to the analyte. For acetone in Figure 7.5a it appears that where there is less PS and less PVP (position 5,5) the $Ra^2$ values are lower, indicating that PGMA has the highest affinity to acetone compared to PS and PVP. Conversely, the largest $Ra^2$ value for acetone is present at position (5,1) at the point of lowest PS graft, but highest PVP graft, resulting in the conclusion that the PVP component has the lowest affinity to acetone.
### Table 7.2 a. Dipole Component Hansen Solubility Parameter for PGMA-PS-PVP gradient.

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### Table 7.2 b. Component Hansen Solubility Parameter for PGMA-PS-PVP gradient.

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### Table 7.2 c. Hydrogen Component Hansen Solubility Parameter for PGMA-PS-PVP gradient.

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Figure 7.5. PGMA-PS-PVP $R_d$ value as a function of geometrical position along the gradients for (a) Acetone, (b) toluene, (c) chloroform, and (d) methanol.
The $Ra^2$ values for toluene (Figure 7.5b) show an opposite trend. In fact, the lowest $Ra^2$ values are present at position (5,1), where there is the most PS grafted and the least amount of PVP grafted. This shows that toluene has a stronger affinity to PS than PVP. The largest $Ra^2$ value is present at position (5,5), where there is the least amount of PS and the largest amount of PVP. This implies that toluene is not a preferential solvent for PGMA, which is the dominant component at that position. Interestingly, chloroform has a similar trend to toluene. Consequently, it appears that chloroform shows the strongest affinity for PS, then for PGMA, and lowest affinity for PVP.

Finally, the $Ra^2$ values for methanol (Figure 7.5d) vary in the complete opposite direction than for toluene or chloroform. Although the $Ra^2$ values for methanol are still tenfold larger than for the other solvents, it has a strong affinity to PVP, due to the hydrogen bonding possibilities, and very little affinity where PGMA and PS chemistries are present. From the data in Section 7.3.2 it is possible to conclude that having orthogonally varying chemical compositions along the sample imparts a unique specificity and selectivity to the system, where each chemical moiety has a different and unique affinity to the various analytes in the environment.

7.3.3 Foaming of 2D gradients

In order to permanently record chemical film-environment interaction events, the material should have shape memory (SM) properties. In order to perform foaming, the gradient films were swollen in a good solvent for all polymers (chloroform, having the largest $Ra^2$ value from Figure 7.5c, frozen in their swollen state and placed on the
temperature regulated sample table. The resulting changes in thickness upon foaming for each point along the gradient are presented in Figure 7.4a-e.

Figure 7.4a-e show very interesting results. It appears that as the amount of PVP in the system decreases, the ability of the system to foam increases. In fact, looking at Figure 7.4e, each point across the profile, in general, foams approximately 4 times more than the profile in Figure 7.4a. In addition, looking at each profile, it is noticeable that each location across the entire sample foams to different extents. From these results it can be concluded that the foaming capability is directly linked to the chemical composition and the cross-linking density resulting from such composition. In fact, interestingly to note, is that, even with the different extents of foaming, the resulting shape memory nanofoam is featureless. In fact, looking at the contour plot of one of the samples in Figure 7.5a, it can be seen that the total foamed thickness across the entire sample was 253.6±15.6 nm even though the foam percent varies from 3% to 56% across the sample (Figure 7.4b).

Consequently, it can be concluded that a 2D two-component gradient shape memory nanofoam was successfully synthesized. The chemical composition varies at each location across the sample and when foamed, the resulting structure is featureless. In addition, the changes in thickness at each step can be monitored by ellipsometry and the morphology with AFM.
A

B

C
Figure 7.4. Foaming of PGMA/PS/PVP systems at each location across the gradient position.
Figure 7.5. Contour plot of the foamed sample surface (a) and the change in foaming % at each location across the sample (b).
7.3.4 Response to Analytes

To understand if the 2D two-component foam is a true shape memory system, various analytes were tested in an individual manner, to understand the degree of response each component is responsible for. The interaction of the foamed gradients with saturated vapor of different solvents of different nature was studied. From Section 7.3.2 it was shown that the solvents selected should have a specific and unique affinity to each position along the gradient. Consequently, based on the $Ra^2$ values in Figure 7.4a-e, acetone was used as it was found to be a good solvent for the anchoring layer, a moderate solvent for PS, and a bad solvent for PVP; toluene was chosen as it was a good solvent for PS, moderate for the PGMA layer, and bad for PVP; vapor chloroform is a solvent specific to all components in the systems, and very similar to the initial environment of liquid chloroform that produced the shape memory; consequently it is of importance to understand if the system can impart difference between the two phases (vapor and liquid) of the initial environment; methanol was selected as it is a good solvent for PVP, but bad for the other components. Finally, a mixture of methanol and toluene was selected to understand the response the nanofoam has if more than one solvent is present in the environment. The system was exposed to each solvent for 40 minutes exactly, in an enclosed cell, to allow time for the solvent to evaporate and reach saturation. Finally, the system was exposed to environment of liquid chloroform used for the foaming to collapse it to its original shape. Ellipsometry was used to determine the change in thickness of the polymer after exposure to each analyte.
In Figure 7. 6a-e the thickness response to acetone, toluene, chloroform vapor, methanol, and 1:1 methonal:toluene mixture is shown (as a percent collapse from the foamed state). The obtained results clearly indicate that the extent of the foam collapsing at different places of the gradients is determined by the thermodynamic quality of the solvent. Consequently, each geometrical position showed a very unique collapsing behavior (or “fingerprint”) as a function of the type of solvent vapor. This implies that the chemical composition determines the level of specificity and sensitivity of the system. For example, in Figure 7. 6b, it is clearly noticeable that the shape memory nanofoam collapses in the direction of the PS gradient; in other words, it collapses to a larger extent where there is more PS and to a lesser extent where less PS is present. Chloroform vapor is the analyte that causes the largest extent of collapse, since it is the one with the highest affinity for all the components, in addition to being similar to the original environment of liquid chloroform. The response due to acetone exposure is most likely due to the PGMA layer response, since acetone has the highest affinity to PGMA versus PS or PVP. The methanol collapse pattern shown in Figure 7. 6d shows somewhat of a trend following the direction of the PVP gradient, since methanol shows affinity with PVP, but it is not as well defined as the trend that PS had with Toluene.

Preliminary results showing the 2D two-component system collapse upon exposure to multiple environments, simultaneously, is shown in Figure 7. 6e. Methanol and toluene were used as a mixture for two main reasons. The first is that they are miscible in each other. The second reason, and the most important, is their affinity to their specific different chemical components in the gradients (methanol for PVP, and
toluene for PS). Further investigation is needed to understand the response of such system to mixtures, but the preliminary results reveal an interesting pattern in the percent collapse at each point across the 2D gradients. Specifically, it is noticeable that, generally, where there is more PVP present in the system, the response is more limited.

It is important to notice that upon exposure to its original environment (liquid chloroform), the thickness goes back to its original state within a 3% error. Consequently, it can be concluded that a successful 2D two-component system gradient shape memory nanofoams material was produced, with high specificity and selectivity. In addition, the extent of response reveals that it is possible to detect and identify the analyte as a function of chemical composition.

7.4 Conclusions

Chapter 7 discusses the synthesis and characterization of a 2D two-component system with PGMA/PS/PVP which was successfully created. The developed thermal stage seemed to work successfully. Ellipsometry and AFM revealed that, anywhere along the sample, the chemical composition ratio between PGMA, PS, and PVP was unique.

The 2D two-component systems were successfully made into SMPs as well. In these systems, it appeared that the extent of foaming was dependent on the amount of PVP in the system. Specifically, as the grafting density of PVP decreases, the foaming extent increases. In addition, it is important to note that each location across the entire sensor foams to different extents. From these results it can be concluded that the foaming capability is directly linked to the chemical composition and the cross-linking density.
Figure 7.6. Contour plots of the individual response (percent collapse) of the 2D two-component gradient shape memory nanofoam to (a) acetone, (b) toluene, (c) chloroform in the vapor phase, (d) methanol, and (e) 1:1 methanol:toluene mixture.
resulting from such composition. Once again, the resulting shape memory nanofoam is featureless.

The response to various analytes was studied as an independent interaction, and not sequential. The results clearly indicate that the extent of the foam collapsing at different places of the gradients is determined by the thermodynamic quality of the solvent. In other words, each geometrical position showed a very unique collapsing behavior as a function of the solvent type. This implies that the chemical composition determines the level of specificity and sensitivity of the system. All systems revealed shape memory characteristics since when exposed to the original environment, the morphology and the thickness went back to their original value.

Finally, Chapter 7 concludes that a successful 2D two-component system gradient shape memory nanofoams material was produced, with high specificity and selectivity. In addition, the extent of response reveals that it is possible to detect and identify the analyte as a function of chemical composition. Specifically, an orthogonal chemical gradient shape memory nanofoam was successfully developed and proved it can be used for unattended sensing purposes.
8 SUMMARY AND FUTURE WORK

8.1 Summary

A new generation of shape memory materials that can selectively and specifically sense multiple environments by irreversibly changing their internal nanostructure was developed. To the best of our knowledge, limited work had been achieved on freeze drying chemically functionalizing SMPs to be able to detect multiple analytes and simultaneously having a specific response. In addition, studying the behavior of functionalized SMPs will impact the field of unattended sensing. An anchoring layer that is swellable yet not soluble with available epoxy groups for further functionalization was created. The anchoring layer was successfully foamed and shows typical characteristics of shape memory materials as they collapse when re-introduced to their original environment. In addition, it is possible to accurately tailor the properties of the films, both for thickness and morphology. Refractive index can be calculated with precision to monitor change in light intensity. The microarray disk resonators were proven to show accurate and specific detection of different analytes for various foamed chemically functionalized systems.

8.1.1 Synthesis and characterization of shape memory nanofoams

Chapter 4 revealed a successful fabrication of shape memory polymer nanofoams with both PGMA and PMMA-co-PGMA polymers, two anchoring layer types with a difference of 70% in epoxy groups. The copolymer, having fewer epoxy groups (cross-linking sites) foamed to a larger extent compared to PGMA. The nanofoams revealed
shape memory behavior due to the fact that, when exposed to their original environment, they collapsed and returned to their original thickness. AFM revealed to be a powerful tool to monitor the change in morphology. Nanotomography experiments determined that the pores in the nanofoams are situated throughout the entire foamed layer. The size of the interconnected and open pores inside is between 10 and 100 nm. The foamed structures appear to swell to a larger extent than before foaming for both polymers and for all solvents analyzed. This phenomenon can be explained by the simple conclusion that the samples are not actually foamed to their maximum extent. Chapter 4 shows that the anchoring layer reveals an imparted selectivity to various analytes. Similarly, selective solvents collapsed the system to a larger extent than non-selective solvents.

In Chapter 4, PMMA-co-PGMA systems undergo a change in refractive index that is much larger than for PGMA systems, proving that the waveguide resonators proved to be a successful detection platform. Concluding, Chapter 4 shows that shape memory nanofoams with imparted selectivity to different environments were synthesized and characterized. In addition, ellipsometry and AFM proved to be accurate methods to monitor the changes in thickness, morphology, and refractive index. Finally, it can be shown that this new platform can be used for further functionalization to impart selectivity and specificity so as to create a very sensitive and efficient sensor, capable of identifying and remembering multiple environments.
8.1.2 Synthesis and characterization of chemically functionalized shapememory nanofoams

Chapter 5 was focused on the fabrication of functionalized shape memory polymer nanofoams. Chapter 5 revealed successful chemical functionalization with both PS-COOH and EA, given the versatile chemistry that the PGMA epoxy groups offer. Chemistries interpenetrate the structure allowing for chemical modification within the entire anchoring layer, allowing for an efficient response. Even when chemically functionalized, the nanofoams reveal shape memory properties. In addition, each analyte acts as a plasticizer causing a localized response (partial collapse) where the functionality is present. In all systems with PMMA-co-PGMA as the anchoring layer, the change in refractive index as a function of change in thickness is much larger than for PGMA systems. Consequently, this implies that PMMA-co-PGMA systems seem more sensitive to the environment. Finally, in Chapter 5, it was shown that the waveguide racetrack resonators prove to be a feasible platform for chemically functionalized shape memory nanofoams for unattended sensing. Interestingly, not all systems show a shift towards higher wavelengths upon exposure to analytes.

8.1.3 Synthesis and characterization of 1D and 2D orthogonal chemically functionalized shape memory nanofoams

Chapter 6 and Chapter 7 discuss the synthesis and characterization of a 1D and 2D one and two-component systems. Mainly, a 2D two-component system with PGMA/PS/PVP was also successfully created. The developed thermal stage seemed to work successfully. Ellipsometry and AFM revealed that, anywhere along the sample, the chemical composition ratio between PGMA, PS, and PVP is unique.
The 1D one and two component systems proved to have shape memory property. According to ellipsometry, the 1D one-component systems foamed up to 15%. The 1D two-component systems foamed up to 9%. AFM images demonstrated changes in structure of the films for both systems. It was noticeable that the amount of foaming increases moving from the PS-poor side to the PS-rich side. In addition, it was possible to achieve a flat foamed surface across the entire geometry of the sample. This is necessary for an effective unattended sensor to efficiently monitor the response to environmental changes. As previously reported, the change in morphology was easily monitored with AFM. The ellipsometric measurements revealed a gradual decrease in thickness of the PS/PGMA gradient after the sequential interaction with methanol and chloroform saturated vapors respectively. The results indicated that the extent of the foam collapse at different places of the gradient is determined by the thermodynamic quality of the solvent. Consequently, it can be said that each geometrical position showed unique fingerprint for each solvent type.

Statistical analysis revealed that, within 95% confidence, there is a significant difference in the variance between acetone and toluene and between toluene and vapor chloroform, confirming that the system has specificity. Statistical analysis did not show a significant variance in the profiles resulting from vapor and liquid chloroform.

The 2D two-component systems were successfully made into SMPs as well. In these systems, it appeared that the extent of foaming was dependent on the amount of PVP in the system. Specifically, as the grafting density of PVP decreases, the foaming extent increases. In addition, it is important to note that each location, across the entire
sensor, foams to different extents. From these results it can be concluded that the foaming capability is directly linked to the chemical composition and the cross-linking density resulting from such composition. Once again, the resulting shape memory nanofoams are featureless.

The response to various analytes was studied as an independent interaction. The results clearly indicate that the extent of the foam collapsing at different places of the gradients is determined by the thermodynamic quality of the solvent. Similarly to a 1D two-component gradient, each geometrical position showed a very unique collapsing behavior as a function of the solvent type. This implies that the chemical composition determines the level of specificity and sensitivity of the system. In addition, all systems revealed shape memory characteristics due to the fact that, when exposed to the original environment, the morphology and the thickness went back to their original value.

Finally, the data in Chapter 6 and Chapter 7 conclude that a successful 2D two-component system gradient shape memory nanofoam material was produced, with high specificity and selectivity. In addition, the extent of response reveals that it is possible to detect and identify the analyte as a function of chemical composition. Specifically, an orthogonal chemical gradient shape memory nanofoam was successfully developed and proved it can be used for unattended sensing purposes.

8.2 Future Work

Recommendations for future work include creating a three and four component orthogonal SMP nanofoam system. Possible functionalities to use include PMMA and
ethanol amine. Functionalities that are hydrophylllic, such as poly(ethylene glycol) (PEG) are not recommended as they would attract moisture in the air and cause a partial collapse due to the environment and not due to a sensing mechanism.

I would recommend testing these nanofoams on waveguide race track resonators for further analysis of the system.

8.3 List of Publications and Presentations

8.3.1 Publications


8.3.2 Conference Presentations and Posters

- Anna Paola Soliani, et al., “Gradient films from shape memory nanofoams for unattended sensing.” American Chemical Society National Meeting, Dallas, TX, March 2014, oral presentation.
- Anna Paola Soliani, et al., “Gradient films from shape memory nanofoams for unattended sensing.” American Chemical Society National Meeting, Dallas, TX, March 2014, poster.
- Yuriy Galabura, Anna Paola Soliani, Bogdan Zdyrko, and Igor Luzinov “Shape memory polymers: grafted nanofoams.” American Chemical Society National Meeting, New Orleans, LA, April 2013, oral presentation