STIMULI-RESPONSIVE MATERIALS FROM THIOL-BASED NETWORKS

by

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For all proprietary information contained therein
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Abstract

by

WILLIAM ALEXANDER BRENN

Future stimuli-responsive materials – “smart” materials – will focus on introducing new types of stimuli responses into materials and creating materials that can respond to several stimuli in different ways. The effect of each of these focuses will be the introduction of many novel materials with a wide range of functionalities and properties. The aim of this work is the synthesis of such materials using thiol-based networks.

The first chapter focuses on an effort to include thermally-responsive shape memory into an aerogel, using a semicrystalline polymer network and Cellulose Nanocrystals (CNCs). The semicrystalline domains of the network served to facilitate the shape fixing of the material and the CNCs were incorporated in an effort to prevent the gel from collapsing out of aerogel form when heated above the crystalline melting temperature.

The second chapter centers on work synthesizing a liquid crystalline elastomer (LCE) using 2,6-bisbenzimidazolopyridine (bip) as the mesogen unit and using dynamic disulfide bonds as the crosslinks. Using bip as the mesogen allows the liquid crystalline transitions to be controlled using temperature, UV light, and exposure to metal ions. Including the dynamic disulfide crosslinks allows the material to be reproccessible, healable, and act as an adhesive.
Chapter 1. Introduction

Stimuli-responsive materials – materials that change their properties in response to one or more stimuli – have received a large amount of attention for their potential in unlocking new technologies\(^1\). Many such “smart” materials have been reported, exhibiting responses such as healing\(^2\)-\(^8\), adhesion\(^9\)-\(^13\), shape memory\(^14\)-\(^18\), and actuation\(^19\)-\(^21\). The aim of this work is to develop novel smart materials from thiol-based networks that introduce new types of stimuli-responses into materials, as well as combining multiple stimuli-responses into one material.

The second chapter of this thesis focuses on an attempt to create a thermally responsive shape memory aerogel, Combining shape memory properties with the porosity, low density, and high surface area properties of aerogels. To this point, no such material has been reported. Such a material could be attractive as a potential expandable insulator for aerospace applications, among other applications.

The goal of the third chapter is to create a multifunctional material by creating a Liquid Crystalline Elastomer (LCE) with dynamic disulfide bonds as crosslinks. LCEs are materials that can act as shape memory actuators where the liquid crystal (LC) domains transition from nematic (ordered) to isotropic (disordered), as shown in figure 1.1. Dynamic disulfide networks allow for reprocessing of crosslinked networks, as well as facilitating adhesion and healing properties\(^22\). Marrying these two can provide access to a material with a wide range of functionalities.
Figure 1.1. LCE actuation mechanism scheme. Chevrons represent the LC mesogens
Chapter 2. Thermally Responsive Shape Memory Aerogels

2.1 Introduction

Aerogels are a specialty material formed by the removal of solvent from a gel while preserving the porous structure of the material. These materials have several attractive properties: low density, high surface area, and low thermal and dielectric constants\textsuperscript{23-25}. The first aerogel was produced by S.S. Kistler in 1931\textsuperscript{26}. Early aerogels were made from inorganic materials, but more recently, organic aerogels from polymers such as polystyrenes\textsuperscript{27,28}, polyimides\textsuperscript{29-34}, polyamides\textsuperscript{35}, and polyurethanes\textsuperscript{36,37} have been synthesized. These polymeric aerogels have superior toughness, deformability, and ability to recover from deformations than their inorganic predecessors, which suggests that shape-memory aerogels may be attainable\textsuperscript{38}. Shape-memory materials can be compressed to a fixed shape and recover to the original state. Shape memory can be triggered by different stimuli, and aerogels have been developed that exhibit shape memory triggered by solvents. To this point, however, no thermal shape-memory materials have been reported. The goal of this research was to create an aerogel from a shape-memory polymer that can hold a fixed shape and recover its aerogel state when heated.

\textbf{Figure 2.1. Schematic representation of thermal shape memory.}
The class of shape-memory polymer investigated here is a crosslinked network that uses a physical transition such as a melting transition ($T_m$) or glass transition temperature ($T_g$) to hold the network in a fixed shape when heated, compressed, and cooled. These materials can then simply be heated above that transition temperature and a drop in modulus allows the network to recover its original shape$^{1,39-42}$.

2.2 Experimental

2.2.1 Materials

1,6-hexanedithiol (HDT), 1,5-hexadiene (hexadiene), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide and N-methyl-2-pyrrolidinone (NMP) were used as purchased from Sigma Aldrich. CNCs were harvested from the cellulose mantles of sea tunicates after hydrolysis with sulfuric acid using established techniques$^{39,40}$. CNC solutions in NMP were produced by adding the solvent to the solid and sonicating until well-suspended (ca. 2 h).

2.2.2 Instrumentation

The UV lamp used for synthesis of the thiol-ene gel was a Bluepoint 4 Ecocure from Honle UV America Inc. Skeletal densities ($\rho_s$) were determined by helium pycnometry using a Micrometrics Accupyc 1340 gas pycnometer. Bulk density ($\rho_b$) was determined by measuring the length and diameter of cylindrical samples to geometrically calculate the volume and then dividing the mass by this result. Porosity ($p$) was then calculated by $p = 100\% \times (1-\rho_b/\rho_s)$. Shape memory testing was carried out on a TA Instruments Q800 DMA equipped with a compression fixture. A cylindrical sample with approximate length and diameter of 3 mm and 10 mm respectively is loaded into the fixture.
The temperature is then raised to 100°C and the sample is compressed with a force of 1.0 N. The deformation is then held while the sample is cooled back to room temperature. Once cooled, the compressive strain is measured (εm, maximum strain). The force on the sample is then released and the compressive strain (εf, fixed strain) is measured. The sample is then heated again to 100°C and allowed to recover, with a compressive strain measurement again taken (εr, recovered strain).

2.2.3 Synthesis of CNC Nanocomposite Aerogels

To create the aerogels, an organogel was synthesized before being subjected to supercritical CO2 extraction to convert it to an aerogel. The organogels were produced by thiol-ene photopolymerization using phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide as the photoinitiator. The crosslink density was set to be 1500 g mol⁻¹/crosslink and the polymer concentration was set to be 200 g/L; these conditions were chosen because they yielded the highest porosity aerogels, based on earlier experiments. The proportions of HDT, hexadiene, and PETMP were set such that [thiol]:[ene] was 1:1. The process for a 0% CNC solution was as follows: PETMP (88.20 mg, 0.180 mmol), HDT (312 µL, 2.074 mmol), hexadiene (200 µL, 2.435 mmol), and the photoinitiator (29.270 mg, .070 mmol) were dissolved in 3 mL of NMP. For the gels with 1.5, 3, 4.5, and 6 wt.% CNCs, the NMP was replaced by 3 mL of CNC dispersions with concentrations of 2.5 mg/mL, 5 mg/mL, 7.5mg/mL, and 10mg/mL, respectively. The reaction mixture was then transferred to a syringe mold – a 5 mL plastic syringe with the tip removed – and exposed to the UV source equipped with a 320-390 nm filter and a 25 aperture at an intensity of ca. 30 mW/cm² for one hour, rotating 90° every 15 min., to ensure even exposure. The gel was then ejected from the syringe into a glass jar and soaked in NMP overnight. Before the gel was able to
undergo supercritical CO₂ extraction, it needed to be solvent exchanged into Acetone, as NMP is not compatible with the process. This process was carried out by soaking the gel in NMP overnight, then soaking in 75:25, 50:50, 25:75, 0:100 NMP:Acetone overnight before soaking in Acetone overnight twice, replacing the Acetone after each day.

2.2.4 Supercritical CO₂ Extraction

Thiol-ene organogels were immersed in either acetone or acetonitrile in a 1L sealed chamber. The chamber was pressurized to 75 bar at a temperature of 25 °C and the gel was continuously washed with liquid CO₂ at a flow rate of 9 g/min for 90 min. The gel was then allowed to soak for 30 min. This wash/soak procedure was repeated three more times. The pressure and temperature of the vessel were then raised to 90 bar and 35 °C respectively and the gel was continuously washed with supercritical CO₂ at a flow rate of 9 g/min for 90 min followed by 30 min of soaking. This wash/soak was repeated one time and then the pressure in the vessel was reduced to atmospheric pressure by venting CO₂ at a rate of 10 g/min. The resulting aerogel was then dried overnight in vacuo to remove any remaining solvent.

2.2.5 Shape Memory Testing

Shape memory testing was carried out on a TA Instruments Q800 DMA equipped with a compression fixture. A cylindrical sample with approximate length and diameter of 3 mm and 10 mm respectively is loaded into the fixture. The temperature is then raised to 100 °C and the sample is compressed with a force of 10 N. The deformation is then held while the sample is cooled back to room temperature. Once cooled, the compressive strain is measured (εₘₐₓ, maximum strain). The force on the sample is then released and the
compressive strain ($\varepsilon_f$, fixed strain) is measured. The sample is then heated again to 100 °C and allowed to recover, with a compressive strain measurement again taken ($\varepsilon_r$, recovered strain).

2.3 Results and Discussion

To access shape-memory aerogels, highly crosslinked semi-crystalline thiol-ene networks with a $T_m$ of the crystalline domains above room temperature were targeted. These were based on 1,5-hexadiene – a diene monomer – and two thiol containing monomers: hexanediol (HDT) – a dithiol – and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) – a tetrathiol crosslinker (figure 2.2). A similar material based on these monomers was reported as an SMP with a $T_m$ of ca. 60 °C.1

A main challenge to overcome in producing such a material is the strain in the polymer matrix when in aerogel form. Since all the chains are stretched out, the matrix tends to collapse upon heating, prohibiting thermal shape-memory. To overcome this, Cellulose Nanocrystals (CNCs) were investigated as a potential means of reinforcing the polymer matrix to create a nanocomposite aerogel. The theory behind creating a nanocomposite aerogel is that the cellulose whiskers will essentially form a scaffold which can aid the gel in keeping its shape when heated. Furthermore, cellulose nanofibril- and nanocrystal-based aerogels have been shown to exhibit shape memory properties triggered by solvent43-45. As well, the whiskers may aid the shape-memory of the gel, by supporting its original shape.

Thiol-ene organogels were synthesized from PETMP, HDT and hexadiene in NMP and in suspensions of CNCs in NMP. The organogels were then solvent exchanged into acetone, as NMP is not compatible with the supercritical CO$_2$ extraction process. Gels were
Figure 2.2. Nanocomposite aerogels are synthesized from HDT, hexadiene and PETMP via photopolymerization in a suspension of CNCs in NMP before being solvent exchanged into Acetone and subjected to supercritical CO₂ extraction produced in NMP and CNC suspensions in NMP to produce aerogels with 0, 1.5, 3, 4.5, and 6 wt.% CNC loading – higher loading was not accessible, as CNCs could not be dispersed in higher concentrations. The aerogels created are shown in Table 2.1.

<table>
<thead>
<tr>
<th>%wt. CNC</th>
<th>Bulk Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Fixing Ratio (%)</th>
<th>Recovery Ratio (%)</th>
<th>Porosity After Testing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.354</td>
<td>67.8</td>
<td>79.9 ± 0.4</td>
<td>11.2 ± 0.3</td>
<td>25.5</td>
</tr>
<tr>
<td>1.5</td>
<td>0.379</td>
<td>65.5</td>
<td>71.4 ± 0.2</td>
<td>12.5 ± 0.1</td>
<td>19.8</td>
</tr>
<tr>
<td>3</td>
<td>0.436</td>
<td>60.3</td>
<td>76.2 ± 0.3</td>
<td>9.8 ± 0.3</td>
<td>27.1</td>
</tr>
<tr>
<td>4.5</td>
<td>0.327</td>
<td>70.2</td>
<td>67.3 ± 0.1</td>
<td>11.4 ± 0.1</td>
<td>24.4</td>
</tr>
<tr>
<td>6</td>
<td>0.419</td>
<td>61.9</td>
<td>65.3 ± 0.1</td>
<td>11.5 ± 0.1</td>
<td>24.5</td>
</tr>
</tbody>
</table>

Table 2.1. Table of Aerogels and their porosities and shape memory testing results
The porosities for all of these materials were calculated assuming a skeletal density of 1.1 g/cm³, as pycnometry data for different samples reliably showed that this was always the skeletal density of these nanocomposites. These materials did not show good shape memory properties, however. The fixing ratios for the first cycle of each of the shape memory tests of these materials, defined as \((\varepsilon_f - \varepsilon_i)/(\varepsilon_m - \varepsilon_i)\), where \(\varepsilon_i\) is defined as the initial strain at the start of the shape memory cycle, were good, between ca. 65 % - 80%. However, the recovery ratios, defined as \((\varepsilon_r - \varepsilon_m)/(\varepsilon_i - \varepsilon_m)\), were very poor, indicating that the aerogels collapsed when heated and compressed. The shape memory graphs are shown in figures A.2.1 – A.2.5. The porosities of these materials after undergoing the shape memory tests confirmed that these materials did indeed collapse to a non-aerogel state during the test.

### 2.4 Conclusions

Nanocomposite aerogels were produced from thiol-ene photopolymerization of 1,6-hexanedithiol, 1,5-hexadiene, and pentaerythritol tetrakis(3-mercaptopropionate) in suspensions of Cellulose Nanocrystals. The resulting aerogels had porosities between ca. 60% and 70%. The materials did not display thermally responsive shape memory, however, collapsing back to a standard gel state after being subject to a 10 N load at 100 °C. Future work will be needed to develop a successful strategy for creating a thermo-responsive shape memory aerogel.
2.5 Appendix

A.2.1. *The first cycle of a thermal compressive shape memory graph for aerogel material with 0 %wt. CNC loading.*
A.2.2. The first cycle of a thermal compressive shape memory graph for aerogel material with 1.5 %wt. CNC loading.
A.2.3. The first cycle of a thermal compressive shape memory graph for aerogel material with 3 %wt. CNC loading.
A.2.4. The first cycle of a thermal compressive shape memory graph for aerogel material with 4.5 %\textsubscript{wt} CNC loading.
A.2.5. The first cycle of a thermal compressive shape memory graph for aerogel material with 6 %wt. CNC loading.
Chapter 3. Metallo-, Thermo-, and Photo-responsive Healable, Shape Memory and Actuating Liquid Crystalline Elastomers and Adhesives

3.1 Introduction

There is great interest in the use of structurally dynamic materials as stimuli-responsive “smart” materials. Such materials usually incorporate a dynamic covalent or supramolecular bond that can undergo a reversible exchange or breaking and reforming process when exposed to a specific stimulus. This structural change offers access to numerous macroscopic changes such as healing, shape memory, actuation, color change, and changes in mechanical properties. A large number of the current generation of these materials are mono-functional: they respond to only one stimulus in one way.

Multi-functional stimuli-responsive materials – materials which react to more than one stimulus or demonstrate more than one response – have received a great deal of attention recently. Particularly, the synergistic nature of shape memory and healing responses has drawn interest to dual shape memory-healable polymers. For example, the shape memory response can be used to facilitate crack closure which aids the healing response. There are two broad categories into which these materials fall: homogeneous and heterogeneous. Homogeneous materials consist of only one material containing dynamic bonds within that material which allow the healing process to occur and a physical transition, the glass transition or melting temperature, to allow the shape memory response. Heterogeneous materials consist of two distinct components, one to facilitate the healing and one to facilitate shape memory.

The utility of multifunctional materials and the potential synergies between multiple functionalities is underscored in recent work by Pei and Coworkers, who
synthesized liquid crystalline elastomer (LCE) networks containing esters throughout the network. They demonstrated that the material can “relax” in a monodomain liquid crystalline state by aligning the liquid crystal mesogens via mechanical stretching then inducing dynamic behavior of the network through a transesterification reaction. This presents a promising solution to a key challenge in producing efficient LCE actuators since the method of producing monodomain LCEs involve aligning the mesogens prior to and during crosslinking, and this can be difficult to achieve. The alignment of the mesogens into a monodomain LCE, aided by the dynamic ester bonds, enhances the actuation response. Thus, one functionality aids the other. Zhang and coworkers developed another example of a dynamic LCE. They utilized a block copolymer with liquid crystalline side chains in one block and hydrogen bonding moieties in the other. The hydrogen bonds served as crosslinks in a healable supramolecular LCE network.

Previous work by the Rowan Group reported a healing and shape memory polymer, with the semicrystalline nature of the polymer facilitating the shape memory response and disulfides facilitating the healing response. Heating the network to above the melting transition of the crystalline domains (T_m of ca. 60°C) allows the network to be deformed to a fixed shape and as it is held in that shape and cooled below the melting temperature, the crystalline domains act as physical crosslinks to hold the material in that fixed shape. Heating the material above the melting temperature again permits elastic recovery to the original shape. The disulfide bonds in the network exhibit dynamic behavior in response to UV light or heat (ca. 150 °C), which allows the network to rearrange and flow. This dynamic behavior facilitates the healing of small scratches/defects in the material. The material can also act as a reversible, stimuli-responsive adhesive. The material can bond
and debond to a substrate when subjected to a stimulus that causes the dynamic behavior of the disulfide bonds (UV light or ca. 150°C). This adhesive can exhibit shape-memory behavior in addition upon exposure to lower temperatures (ca. 80°C) while the adhesive can also exhibit shape-memory properties upon exposure to lower temperatures (ca. 80°C).

Additionally, Rowan and coworkers demonstrated that LCEs constructed from a derivative of a 2,6-bisbenzimidazolylpyridine (Bip) ligand as a thermotropic mesogen and thiol-ene chemistry – that is not structurally dynamic – can act as a thermo-, photo-, and metallo-responsive shape memory material and actuator. The photo-induced LC to isotropic transition occurs because the Bip moiety acts as a chromophore, absorbing UV light and converting it to heat. The metal response occurs as a result of the bonding of the metal ion to the ligand, which then changes the conformation of the molecule and “switches off” its mesogenic behavior. Hence, the LC transition can be activated by heat, light or metal ions, so shape memory and actuation can be accessed via all three of those stimuli. Because these materials are not dynamic, they cannot be reprocessed into different shapes or aligned after crosslinking. The goal of this research is to combine the dynamic character of the self-healing network with the LC behavior of the Bip network in order to expand the functionalities of the material. As a result, the structurally dynamic LCE should act as an LCE and self-heal in response to heat and light and act as a stimuli-responsive adhesive.

3.2 Experimental

3.2.1 Materials

3.1 was prepared according to literature procedures. All solvents were purchased from Fisher Scientific. All other chemicals and reagents were purchased from Sigma-Aldrich Co. Reagents were used without further purification.
3.2.2 Instrumentation

The UV lamp used for the synthesis of the bisthiol oligomer 3.2 was a Bluepoint 4 Ecocure from Honle UV America. NMR data were recorded on a Varian Inova 600 MHz NMR spectrometer. The Melt press used was a Carver Laboratory Press Model C equipped with a Systag TCU-82 temperature control.

3.2.3 Synthesis of Dynamic LCE Network

3.1 (332 mg, 0.619 mmol), 1,6-hexanediathiol (HDT) (171 µL, 1.12 mmol), and phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (30 mg, 0.070 mmol) were dissolved in dichloromethane (DCM, 3 mL) in a 20 mL vial with a stir bar. The sample was then stirred while being exposed to a light source equipped with a 320-390 nm filter and irradiated for 2 hrs at an intensity of 50 mW/cm². An aliquot was taken from the reaction, dried under vacuum to remove any residual 1,6-hexanediathiol, and used for NMR analysis before being added back to the reaction mixture. The reaction mixture was then dried under reduced pressure and pentaerythritol tetrakis(3-mercaptopropionate) (PETMP, 15 mg, 0.031 mmol) was added to the vial. The contents of the vial were then dissolved in 3 mL tetrahydrofuran (THF) and transferred to a 10 mL beaker and 0.1 mL of a 10mg/mL aqueous solution of NaI was added. Finally, 5 drops of 30% aqueous hydrogen peroxide were added to the beaker while stirring. After approximately 3 mins the solution turned redish brown – indicative of the iodide being converted to iodine – and gelation was observed. The resulting gel was washed three times with dichloromethane to remove any unreacted monomer and photoinitiator. Then the gel was washed with 5 wt.% aqueous sodium thiosulfate to remove any remaining iodine. This was followed by one final wash with water. The resulting gel was then dried overnight under vacuum and then compression
molded at 140 °C for 30 mins using an applied force of 4 metric tons between Poly(tetrafluoroethylene) sheets. The resulting film had a thickness of approximately 300 µm and had a light brown hue, possibly as a result of residual Iodine.

3.3 Results and Discussion

A dynamic LCE was synthesized as shown in scheme 3.1. A bisthiol oligomer, 3.2, was prepared via a thiol-ene reaction of 3.167,69 with HDT, ensuring thiol endgroups by using an excess of HDT. NMR analysis, shown in A.3.1, was used to determine the molecular weight of 3.2, by comparing the number of protons adjacent to sulfur groups to protons from a known peak from 3.1 in order to determine the ratio of 3.1 to HDT derived repeat units in 3.2. Knowing this ratio, the molecular weight of 3.2 was calculated to be 1030 g/mol. A small amount of oxidation of the thiol groups to disulfides during the reaction was indicated by a small peak at 2.7 ppm in the NMR spectrum. This was considered inconsequential, as all thiols would be oxidized in the next step. 3.2 was then crosslinked with PETMP by oxidative coupling of thiol groups (with NaI and H2O2)70 to produce a disulfide containing dynamic LCE network 3.3. A molar ratio of ca. 16:1 [3.2]:[PETMP] was used which gives a theoretical molecular weight between crosslinks of
Scheme 3.1. Scheme for producing dynamic LCE network. 3.1 was photopolymerized with HDT to create a bisthiol mesogen, 3.2. This was then crosslinked using PETMP to create a disulfide-containing, dynamic LCE network, 3.3.

8000 g/mol. The overall gel fraction of the material was 93% (dried mass of gel/total mass of monomers and crosslinker).

To demonstrate the shape memory, adhesive, and actuating properties of the material, it was molded into a permanent shape that resembles a claw with flat tabs on the ends of the arms, as shown in figure 3.2, following a procedure outlined in A.3.2. The material was then heated to 60 °C – above the liquid crystalline clearing temperature – and the arms and tab were stretched out and held stretched while cooling to RT. During cooling, the material returned to its LC state, “locking in” the temporary shape, shown in figure 3.2. This shape was then placed over a hot plate at a height so that, when the arms were in their permanent shape with the tab in its temporary shape, the arms would hang just above the hot plate surface, in order to make contact with an aluminum cube placed on the hot plate.
Figure 3.2. Permanent (a) and temporary (b) shape created for shape memory, adhesion, and actuation experiment. (c-f) demonstration of shape memory, adhesive, and actuating properties of the material. Black line shows where bottom of cube sits on plate, red line shows where tab begins in the experiment, before it actuates.

This height was about 4 cm. An aluminum cube, a 2 cm tall piece cut from a profile that is 0.75 x 0.0625 in wide and thick, with a mass 2.079 g, was placed on another hot plate at 160 °C. The hot plate with the claw shape over it was then turned on so that it would slowly heat to about 65 °C in about 5 minutes. As the arms of the claw were heated above the LC clearing temperature – ca. 60 °C – the shape memory of the material was activated and they slowly returned to their permanent shape. Just before the opening between the arms became too small to fit the aluminum cube between them, the cube was transferred from the other hot plate to between the arms of the claw, when the temperature
of the hot plate reaches about 55 °C. The arms of the claw continued returning to their permanent shape, applying pressure on the cube while at a temperature above the temperature where the disulfide crosslinks become dynamic – ca. 150 °C. As the material presses against the cube while above this temperature, it adheres to the cube. Once the arms return fully to their permanent shape (which occurs when the hot plate temperature reaches about 65 °C, The hot plate was turned off and the temperature at the surface of the hot plate was allowed to cool to ca. 30 °C (about 15 minutes). A heat gun aimed slightly above the claw tab (so as not to physically blow on the material) was then turned on to heat the tab above the LC clearing temperature, at which point the tab actuated and lifted the aluminum cube off the hot plate. This process is illustrated in figure 3.2.

3.4 Conclusions

A multi-functional material has been made by incorporating 2,6-bisbenzimidazolylpyridine ligands into a disulfide network to create a dynamic LCE network. The material has been show to combine adhesive, shape-memory, and actuating properties. These properties were demonstrated by the material bonding to an object and using its actuator to physically lift the object up. The incorporation of these three functionalities allows this material to act in novel and innovative ways, including shape-changing glues and actuating coatings or tapes.
3.5 Appendix

A.3.1. 1H NMR spectrum of 2.2 showing the peaks used to determine the ratio of Bip units to sulfur in the oligomers. This ratio can be used to calculate the molecular weight of the oligomer.
Procedure for Creating Claw Demonstration Sample

1. Mold material into flat shape in the melt press using the metal mold shown in A.3.3:
   a. Melt press T: 150 °C
   b. Pressure: 4 metric tons
   c. Time: 30 min.
   d. Allow sample some time to cool in mold to ca. 50 °C before removing from mold.
2. Set melt press so bottom plate is at 150 °C.
3. With tweezeers, press one end of claw onto teflon sheet on melt press to create a tab perpendicular to claw arm. See A.3.4.
4. Take off press, hold folded tab at the end of claw to a flat surface to cool and fix at close to 90° angle to claw arm. See A.3.5.
5. Perform steps 3-4 with other arm of claw, bending tab in opposite direction
6. Allow sample to cool to RT.
   To eliminate permanent twist introduced in steps 3-5:
7. With melt press at 150°C, place sample in mold with ends of the claw arms hanging out. Set pressure to 0.5-1 metric tons. More pressure results in material flowing out from the melt press and creating a buildup of material on the arms. See A.3.6.
   a. Place tweezers or some object on tab pointing upwards to prevent gravity from pulling tab down.
8. Immediately turn temperature down to ca. 50 °C. Let cool to this temperature.
9. Remove sample from mold.

A.3.2. Procedure for creating the claw shape used in demonstration of shape memory, adhesive, and actuating properties of the material.
A.3.3. Top view of mold used to make flat shape, as well as a CAD drawing of the mold.
A.3.4. Molding the perpendicular tab on one arm of the claw.
A.3.5. Cooling to fix the tab perpendicular to the arm on the claw.
A.3.6. Flattening the permanent claw shape. Tweezers are placed to prop up the left tab, which is folded upwards. The right tab is folded downwards.
Chapter 4. Conclusions

The aim of this work was to create novel, stimuli-responsive materials from networks with a thiol-based crosslinker. In chapter one, the goal was to create a thermally-responsive shape memory aerogel from a semicrystalline polymer network, using the $T_m$ as the trigger for shape fixing and recovery. CNCs were used as a strategy to prevent the material from collapsing out of aerogel form when pressed into a fixed shape; the CNC loading in the materials, however, did not aid in the shape recovery of the materials. Different strategies to aid the recovery of the material are needed, potentially the use of an amorphous material – using the $T_g$ as a trigger of shape fixing and recovery. Chapter two details work on a dynamic LCE network created using disulfide bonds as crosslinks. This dynamic character allowed the material to be reproprocessable, in addition to acting as an adhesive, shape memory, and actuating material. The combination of LCE characteristics with dynamic character create the potential for a broad array of new actuating materials, with complex and multi-faceted actuating responses. Such stimuli-responsive materials have tremendous capabilities as future “smart” materials. They can unlock a range of complex activity and meet new applications, above and beyond what current materials can achieve.
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