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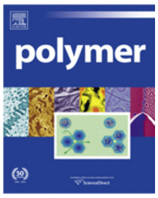

Photopolymerized thiol-ene systems as shape memory polymers

Devatha P. Nair [a], Neil B. Cramer [b], Timothy F. Scott [a], Christopher N. Bowman [b,c], Robin Shandas [a,d,e,*]

[a] Department of Mechanical Engineering, University of Colorado, Boulder, CO, USA
[b] Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO, USA
[c] Department of Restorative Dentistry, University of Colorado, Denver, CO, USA
[d] Deptartment of Pediatric Cardiology, University of Colorado, Denver, CO, USA
[e] Department of Bioengineering, University of Colorado, Denver, CO, USA

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In this study we introduce the use of thiol-ene photopolymers as shape memory polymer systems. The thiol-ene polymer networks are compared to a commonly utilized acrylic shape memory polymer and shown to have significantly improved properties for two different thiol-ene based polymer formulations. Using thermomechanical and mechanical analysis, we demonstrate that thiol-ene based shape memory polymer systems have comparable thermomechanical properties while also exhibiting a number of advantageous properties due to the thiol-ene polymerization mechanism which results in the formation of a homogeneous polymer network with low shrinkage stress and negligible oxygen inhibition. The resulting thiol-ene shape memory polymer systems are tough and flexible as compared to the acrylic counterparts. The polymers evaluated in this study were engineered to have a glass transition temperature between 30 and 40 °C, exhibited free strain recovery of greater than 96% and constrained stress recovery of 100%. The thiol-ene polymers exhibited excellent shape fixity and a rapid and distinct shape memory actuation response.

1. Introduction

Shape memory materials are materials that, after deformation, are able to recover their initial shape upon exposure to a designated stimulus, such as temperature change. The reversion of a deformed shape memory material to its original shape upon heating has a vast range of potential applications in biomedical devices. For example, the shape memory alloy (SMA) Nitinol has been used extensively in implantable biomedical devices, particularly in stents, as the capacity for collapsing an otherwise unwieldy device and returning it to its original shape *in situ* enables minimally-invasive delivery approaches for device implantation [1]. SMA-based devices have several drawbacks associated with high materials cost, limited thermomechanical property control and limited fatigue resistance. Additionally, the maximum strain that can be stored and recovered by SMAs is limited to approximately 8%, which limits the ability of SMAs to be used in certain applications [2,3].

The shape memory capabilities that have been demonstrated in polymeric materials, on the other hand, are extremely versatile. Given the design flexibility that is possible through appropriate formulation of polymer networks and composites, shape memory polymers (SMPs) are designed to meet a wide range of thermomechanical property specifications, including strain deformations of up to 800% [2]. SMPs possess several additional advantages in comparison to SMAs including excellent processability, low relative density, and exceptional flexibility in material property tunability [2–5]. These inherent polymeric material advantages have been exploited in several SMP-based biomedical applications, including the use of degradable SMPs to eliminate the need for any implant removal procedures [5]. Additionally, since the crosslinked polymer's modulus in its rubbery state is primarily dictated by the crosslink density, this modulus is readily tuned to match the tissue modulus at the implant site or another desired specification [5,6]. Further, implanted polymeric devices may also act as convenient drug-delivery vehicles where therapeutic agents are readily incorporated in polymeric matrices that enable subsequent and targeted drug-delivery [6]. One significant drawback of a polymer based SMM is the low modulus it achieves following shape change. The poor mechanical strength of the current shape memory polymer systems in its rubbery state prevents implementation in a number of potential biomedical applications where high modulus post-deployment is required.

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* Corresponding author at: Department of Bioengineering, University of Colorado, Denver, CO, USA. Tel.: +1 720 777 2586.
E-mail address: robin.shandas@ucdenver.edu (R. Shandas).

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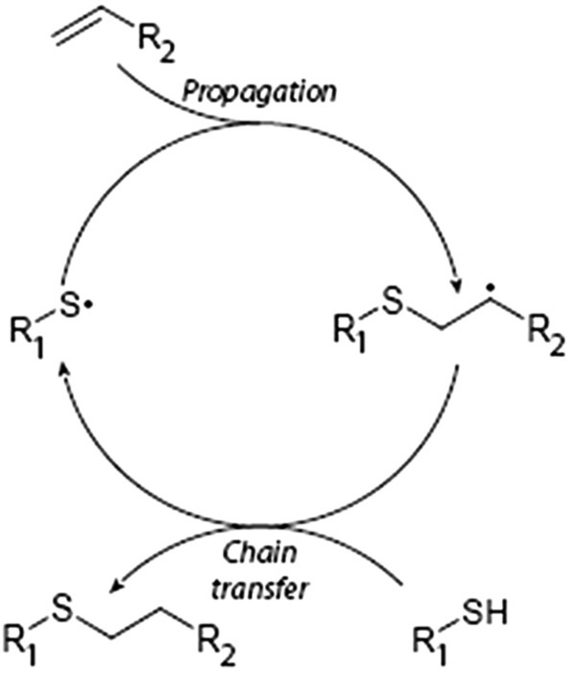
Processing polymers to transform them from their temporary shape to their 'permanent' shape is also relatively simple when compared to metal alloys. Casting an SMP in its transient, typically condensed shape is achieved simply by heating the polymer above its glass transition temperature (T_g), deforming it into its desired transient form, and then quenching the polymer in this transient shape to a temperature below its T_g. Once the polymeric material is again heated to a temperature near or exceeding its T_g, the deformed polymer reverts to its original, desired final shape. SMPs are readily designed to have a varying range of transition temperatures over which the shape change response occurs. By contrast, in alloys, programming the material into its temporary shape involves processing at much higher temperatures and high pressure [2,3].

Photopolymerized (meth)acrylates represent an exciting class of SMP systems [7–10]. The ability to control the polymerization and initial polymer shape readily through photoinitiated polymerization is attractive from both the design and manufacturing perspectives. One particularly attractive option is that photopolymerization, because of the spatial control of initiation and polymerization, facilitates rapid prototyping of patient-specific devices *via* stereolithography. These systems include the use of *tert*-butyl acrylate/diethyleneglycol diacrylate/poly(ethylene glycol) dimethacrylates [7–10], oligo(ε-caprolactone) dimethacrylate/*n*-butyl acrylate [10] and polyurethane-based acrylic systems [11,12]. Shape memory hydrogels have also been developed from acrylic-based monomer systems [13]. Significant limitations of the (meth)acrylate-based systems include the formation of a heterogeneous polymer network with a broader than desired temperature range for the glassy to rubbery transition as well as inhibition of the polymerization by oxygen which restricts design and manufacturing options.

Thiol-ene systems on the other hand offer a unique combination of properties that are advantageous for shape memory polymer systems, including rapid polymerization, low volume shrinkage and shrinkage stress, the formation of homogeneous networks, and insensitivity to oxygen inhibition [14–23]. Thiol-ene systems polymerize uniquely *via* a radical-mediated, step-growth mechanism whereby a thiyl radical adds across a vinyl functional group to generate a carbon-centered radical. The carbon-centered radical undergoes subsequent chain transfer to a thiol group, regenerating the thiyl radical [15,17]. This successive addition/chain transfer mechanism is presented in Scheme 1. The geometric molecular weight evolution resulting from a step-growth polymerization mechanism leads to the formation of a more homogeneous polymer network that results in a relatively narrow glass transition temperature range [17]. The application of thiol-ene systems as shape memory materials for medical devices has not been previously described and is the motivation of this study.

For biomedical devices, it is desirable to actuate the SMP thermally using physiological temperatures. In such applications, the deployment of the device occurs typically from a compressed state packaged at ambient temperature. Following deployment into the desired location, the device is exposed to higher physiological temperatures and reverts to its initial, desired shape.

There are a variety of necessary device design criteria for successful implementation of a shape memory polymer within a biomedical device. The thiol-ene shape memory polymer systems examined here were designed to respond to temperature changes as the stimulus for their shape change. In this work we have characterized shape memory polymer properties and shape memory response by evaluating tensile strength, the glass transition region, free strain recovery, shape fixity, shape recovery sharpness, constrained stress recovery, and shape recovery. The glass transition region defines the temperature and range over which the polymer actuates. Free strain recovery, shape fixity, shape recovery sharpness, constrained stress recovery, and shape recovery are all measures of the polymer's ability to recover its original shape from a temporary shape.



Scheme 1. Radical step-growth polymerization mechanism of thiol-ene photopolymerization reactions.

2. Experimental

2.1. Materials

Diethylene glycol dimethacrylate (DEGDMA), poly(ethylene glycol 575) dimethacrylate (PEGDMA), and *tert*-butyl acrylate (tBA) were obtained from Sigma–Aldrich. The acrylic control used in this study was a known shape memory polymer system that consisted of 49 wt% *tert*-butyl acrylate (tBA), 0.5 wt% diethylene glycol dimethacrylate (DEGDMA), and 49.5 wt% PEGDMA (tBA/PEGDMA) [7,8]. Allyl pentaerythritol (APE) was donated by Perstorp, pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics, isophorone diisocyanate (IPDI) was donated by Bayer, the photoinitiator Irgacure 651 (2,2-dimethoxy-2-phenylacetophenone) was donated by Ciba Specialty Chemicals, and the inhibitor aluminum *N*-nitrosophenylhydroxylamine (*N*-PAL) was donated by Albemarle.

Isophorone diurethane thiol (IPDUT) and isophorone diurethane-6-allyl ether (IPDU6AE) were synthesized by a procedure adapted from Hoyle and co-workers [18,19]. IPDUT was synthesized by mixing one equivalent of isophorone diisocyante with two equivalents of pentaerythritol tetra(3-mercaptopropionate) and 0.05 wt% triethyl amine as a catalyst. The mixture was held at 60 °C until the isocyanate group was reacted to greater than 99% as determined by monitoring the infrared isocyanate peak at 2260 cm^{-1}. The reaction forms a series of oligomers with the idealized, average product shown in Fig. 1. IPDU6AE was synthesized from a reaction of one equivalent of isophorone diisocyanate with two equivalents of allyl pentaerythritol (APE) with 0.05 wt% dibutyl tin dilaurate as the catalyst. The mixture was held at 60 °C until the isocyanate group was reacted to greater than 99% as determined by monitoring the infrared isocyanate peak at 2260 cm^{-1}. Structures for all monomers utilized in this study are shown in Fig. 1.

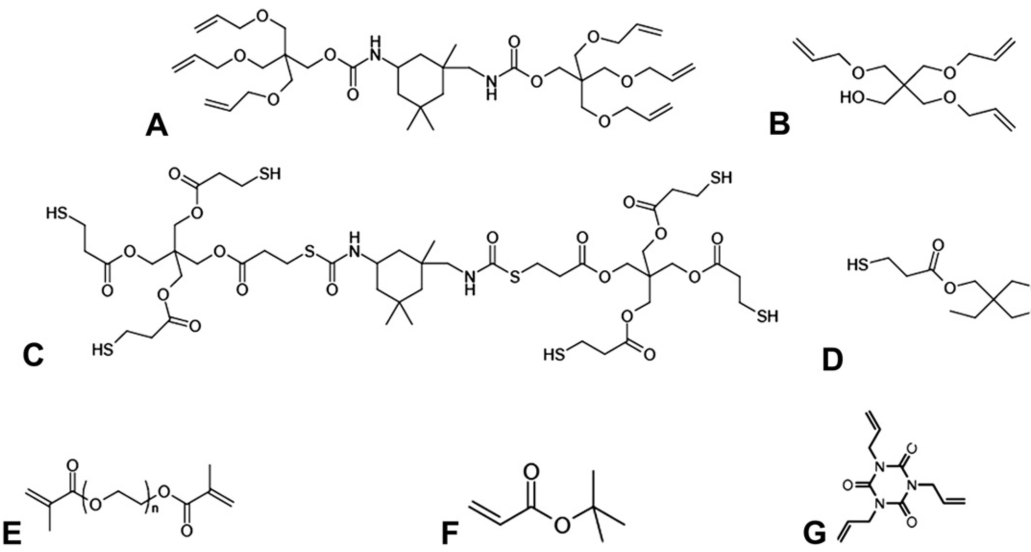


Fig. 1. Monomers used: (A) isophorone diurethane-6-allyl ether (IPDU6AE); (B) allyl pentaerythritol (APE); (C) isophorone diurethane thiol (IPDUT); (D) trimethylolpropane tris(3-mercaptopropionate) (TMPTMP); (E) diethylene glycol dimethacrylate (DEGDMA, $n = 2$) poly(ethylene glycol 575) dimethacrylate (PEGDMA, $n_{avg} = 13$); (F) *tert*-butyl acrylate (tBA) and (G) triallyl-1,3,5-triazine-2,4,6-trione (TATATO).

The thiol-ene systems were all mixed as 1:1 stoichiometric mixtures of thiol to ene functional groups. Samples contained 1 wt% Irgacure 651, 0.1 wt% *N*-PAL and were cured at 8 mW/cm^2 using a UV lamp (Black-Ray Model B100AP).

2.2. Polymer coil fabrication

A mold for the fabrication of polymer coils consisted of a threaded Teflon cylinder inserted in a tight-fitting glass tube. The formulated resin mixture was introduced into the mold and was photopolymerized *in situ* using a UV lamp (Black-Ray Model B100AP). After curing, the glass tube was broken and the polymer was carefully removed from the mold.

2.3. Shape memory programming and recovery

The coils were heated to 10 °C above their T_g and programmed into their temporary, extended tube-like shape by constraining them inside a straight catheter tube. The polymer was cooled to −5 °C in a freezer and was held within the tube for one week in this extended geometry. The polymer was then removed from the tube, observed at room temperature and then placed in an oven maintained 10 °C above the T_g of the polymer. The time taken for the polymer to revert to its original shape was recorded by visual observation.

2.4. Dynamic mechanical analysis (DMA)

DMA experiments were performed using a TA Instruments Q800 DMA.

Glass transition temperature (T_g) was determined from polymer samples with dimensions 7 × 3.5 × 1 mm. Sample temperature was ramped at 3 °C/min from −15 to 75 °C with a frequency of 1 Hz and a strain of 0.05% in tension. The T_g was assigned as the temperature at the tan δ curve maximum. The rubbery modulus values were determined at a temperature 25 °C above the $T_g$and the T_g width was measured as the full width at half height (FWHH) of the tan δ peak.

Free strain recovery, shape fixity and shape recovery sharpness were determined from fully cured samples with dimensions of 10 × 5 × 1 mm. For the free strain recovery tests, the polymers were held at a temperature 5 °C above the T_g of the system and strained in tension between 10 and 20 percent (always making sure to stay within the linear regime). The maximum strain was noted as ϵ_m. While maintaining the strain, the polymers were cooled to −10 °C at 20 °C/min. The force was then maintained at zero and the strain on unloading the polymer was recorded (ϵ_u). The strain recovery was observed as the temperature was increased to 25 °C above the T_g at the rate of 3 °C/min. The final strain of the system postrecovery was recorded as ϵ_p. Free Strain recovery was defined as $R_r(\%) = (\epsilon_u - \epsilon_p)/(\epsilon_m - \epsilon_p)\times 100$. Shape fixity is given by $R_f(\%) = (\epsilon_u/\epsilon_m)\times 100$ and shape recovery sharpness defined by $\nu_r = R_r/\Delta T$, where ΔT is a measure of the width of the transition and is the temperature range from the onset of the recovery to its to completion.

Constrained stress recovery was determined from cylindrical samples measuring 9 mm in diameter and 9 mm in length. Samples were strained in compression at 10% at a rate of 1×10^{-3} s^{-1} at T_g. Samples were subsequently cooled to −10 °C and held for 30 min. At the end of this period, the force applied on the sample was removed. The sample was then heated at the rate of 2 °C/min back

Table 1
Coil and mold diameter and percent resemblance to mold for shape memory polymers.

Formulation	Teflon mold diameter (mm)	Initial coil diameter (mm)	Coil diameter after programming (mm)	Percent resemblance to mold after programming
tBA/PEGDMA	22 ± 1	25 ± 1	26 ± 2	118%
TMPTMP/TATATO	22 ± 1	21 ± 1	21 ± 1	97%
TMPTMP/IPDU6AE	22 ± 1	22 ± 1	22 ± 1	100%
IPDUT/IPDU6AE	22 ± 1	19 ± 2	22 ± 1	101%
IPDUT/APE	22 ± 1	21 ± 1	21 ± 2	97%

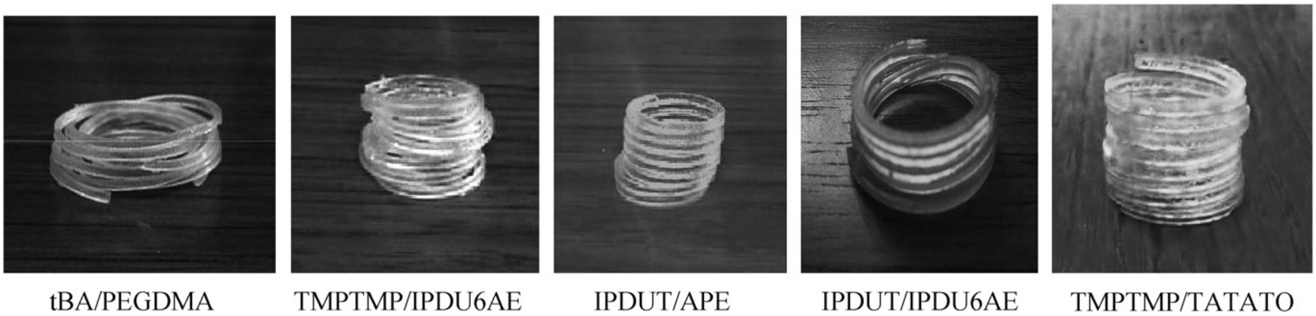


Fig. 2. Images of polymer coils after removal from the teflon mold.

to its T_g and maintained at this temperature for 30 min. The stress exerted by the polymer at its T_g was measured.

2.5. Materials testing system (MTS)

Tensile strength measurements were conducted on an Instron Universal Testing Machine (Insight 2.0). Dog bone shaped samples of dimensions 40 × 6.5 × 1 mm were used. The initial separation of the system was set at 30 mm and a crosshead speed of 3 mm/min was applied.

3. Results and discussion

This work evaluates four different thiol-ene polymer systems in comparison with a conventional acrylic polymer shape memory system as a control. The polymer systems chosen for this study are significantly different in their network structures although all exhibited glass transition temperatures in the range of 30–40 °C, making them suitable for thermally induced biomedical shape memory applications. The acrylic control polymer system was a previously examined shape memory polymer comprised of t-butyl acrylate and polyethylene glycol dimethacrylate. To obtain thiol-ene polymer systems with T_gs near physiological temperature, a tri-thiol (trimethylolpropane tris3-mercaptopropionate) (TMPTMP) and a tri-ene, triallyl-1,3,5-triazine-2,4,6-trione (TATATO) resin was formulated. Additionally, urethane thiol-ene systems have been demonstrated to exhibit excellent mechanical properties and higher elongation at break [17–20]. Therefore, several urethane thiol-ene systems were also examined. Polyurethanes impart improved toughness to polymers and also have a history of use in shape memory polymers and a record of proven biocompatibility [11,12].

Each of the polymer systems was examined for shape memory programming and shape retention. The results are given in Table 1. A comparison of the coil diameter with the mold diameter is detailed to reflect the initial state of the polymer system. Images of polymers after removal from the mold are shown in Fig. 2. Subsequently, the polymers were programmed to their temporary shape and then thermally stimulated by heating to 10 °C above their T_g to regain their original shape. The coil diameter was again observed and the percent change from the mold diameter calculated. Fig. 3 depicts the procedure by which polymer coils are released from their constrained temporary shape at ambient temperature and subsequently heated to a temperature above their T_g. Ideal shape memory polymer systems will exhibit coil diameters closely resembling that of the mold both before and after programming. For biomedical applications such as cardiovascular stents, shape retention is extremely important to prevent leakage around the edges of the polymer. In comparison with the control tBA/PEGDMA system, the thiol-ene systems exhibit better mold retention both before and after programming and a more rapid and distinct shape memory response (by visual observation). Additionally, the TMPTMP/TATATO and the urethane-based thiol-ene systems exhibited excellent toughness as qualitatively determined by their ability to be handled and manipulated without breaking, particularly during mold removal from tightly wound coils. Also, the smallest acrylic coil that could be made from the mold was limited to ≥1 mm while acrylic coils of smaller diameters broke repeatedly

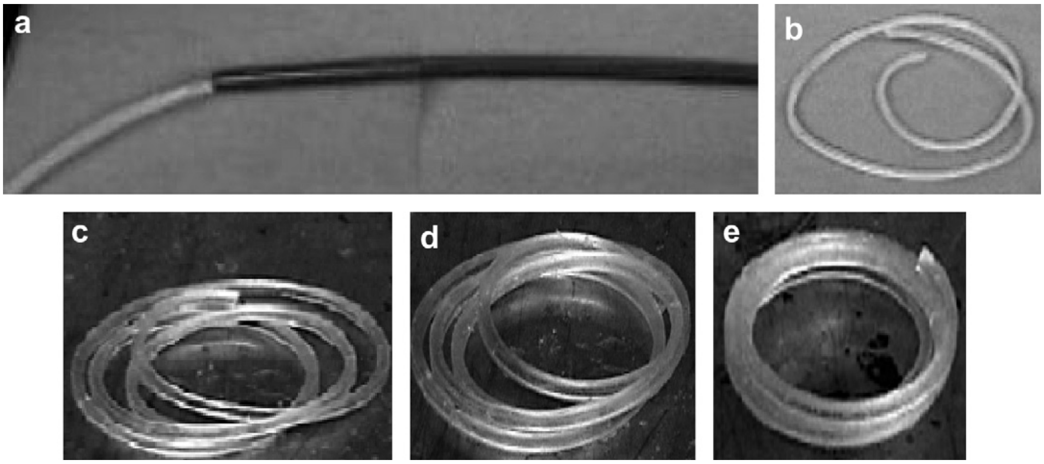


Fig. 3. The process followed to quantify shape memory behavior is outlined in the coil images of the IPDUT/APE polymer system. (a) The polymer coils are heated to 10 °C above their $T_g$and then constrained in tubing. The polymers are then cooled below their T_g to −5 °C and stored for 1 week in the tubing. (b) The polymers are released from the tubing at ambient temperature, where upon they were observed for 4 min. Polymers were then placed in an oven maintained 10 °C above their T_g. The time taken for the coils to form was recorded. Coil images were recorded at (c) 4 min, (d) 4.5 min, and (e) 5 min.

Table 2
Rubbery moduli at $T_g + 25$ C along with T_g and T_g width of the shape memory polymer systems.

Formulation	Rubbery modulus (MPa)	T_g (°C)	T_g width (°C)
tBA/PEGDMA	12 ± 1	35 ± 3	24 ± 4
TMPTMP/TATATO	17 ± 1	36 ± 2	12 ± 2
IPDUT/APE	19 ± 4	33 ± 3	18 ± 3
IPDUT/IPDU6AE	7 ± 1	35 ± 3	30 ± 2
TMPTMP/IPDU6AE	17 ± 3	34 ± 4	25 ± 3

Table 3
Modulus and strain at break for each of the shape memory polymer systems studied.

Formulation	Tensile modulus (MPa)	Strain at break (mm/mm)
tBA/PEGDMA	10 ± 1	1.0 ± 0.2
TMPTMP/TATATO	63 ± 10	0.2 ± 0.1
IPDUT/APE	19 ± 4	0.7 ± 0.1
IPDUT/IPDI6AE	55 ± 1	1.0 ± 0.1
TMPTMP/IPDU6AE	12 ± 1	0.6 ± 0.3

upon attempting to remove them from the mold. In contrast, all of the thiol-ene coils of diameter 0.5 mm were readily produced and removed from the mold.

Table 2 details the rubbery storage moduli and glass transition temperatures of the polymer systems evaluated in this study. Shown in Fig. 4 is a representative storage modulus and tan δ versus temperature curve of the control tBA/PEGDMA system and the TMPTMP/TATATO system. As seen in Fig. 4, the modulus decreases rapidly as the polymer is heated through the glass transition. It is this decrease in modulus that enables mobility within the polymer thereby inducing the shape memory actuation. The tan δ curves demonstrate that the T_g of the urethane thiol-ene polymer systems are comparable to that of the tBA/PEGDMA control. The rubbery moduli of the TMPTMP/TATATO, IPDUT/APE and the TMPTMP/IPDU6AE are all higher than the control and exhibit better mold retention than the tBA/PEGDMA system. However, the IPDUT/IPDU6AE system exhibits the lowest rubbery modulus while still exhibiting much better mold retention than the tBA/PEGDMA system. The narrow T_g width (12 °C) of the pure thiol-ene system, TMPTMP/TATATO indicates the formation of a homogeneous polymer; however, the urethane thiol-ene system exhibits a T_g width that is comparable to the acrylic control system.

Table 3 details the polymer tensile modulus and strain at break of the polymer systems. This test was performed at room temperature to determine how the systems would fare in typical ambient conditions under which the systems may be subject to processing and manufacturing events. Given the narrow T_g width of the TMPTMP/TATATO system, this polymer system was relatively glassy at ambient temperature (23 °C) and exhibited a higher tensile modulus (63 MPa) in comparison to the other polymer systems. The range of moduli of biological tissue can vary from 20 GPa (bone) [24] to 1 kPa (eye) [25]. As the modulus values of biomedical implants and devices are normally engineered to match the immediate *in vivo* environment surrounding the material, this measure also provides information on the scope of potential applications for each material. Although the urethane thiol-ene systems exhibited a uniformly strong shape memory response, there were no concomitant modulus and elongation properties of the polymers correlating directly to the enhanced shape memory behavior (Table 4).

Free strain recovery was also characterized for each of the polymer systems. Free strain recovery is a measure of the ability of the polymer system to recover its permanent shape in the absence of mechanical load as a function of increasing temperature or time. The control polymer system showed a free strain recovery of 96% and the thiol-ene networks exhibited essentially identical free strain recoveries of 97%. The shape fixity of the polymer systems is an indication of the ability of the polymer network to store a temporary shape at a temperature that is below the transition region. From an application point of view, this measure is an indication of the materials ability to store strain energy within the polymer network before the device is activated. All systems evaluated consistently showed shape fixity of ~97%. The shape recovery sharpness gives an indication of the breadth of the transition within which the polymer system would go from its temporary stored shape to its permanent shape. Larger shape recovery sharpness and a narrow strain recovery transition width indicate a rapid transition of the polymer from its stored shape to its final shape. Based on the narrow T_g width and the polymer network homogeneity that results from the thiol-ene reaction mechanism, the thiol-ene system TMPTMP/TATATO demonstrated a rapid recovery level of 5%/°C when compared to the urethane thiol-ene systems and the control acrylic system. The shape

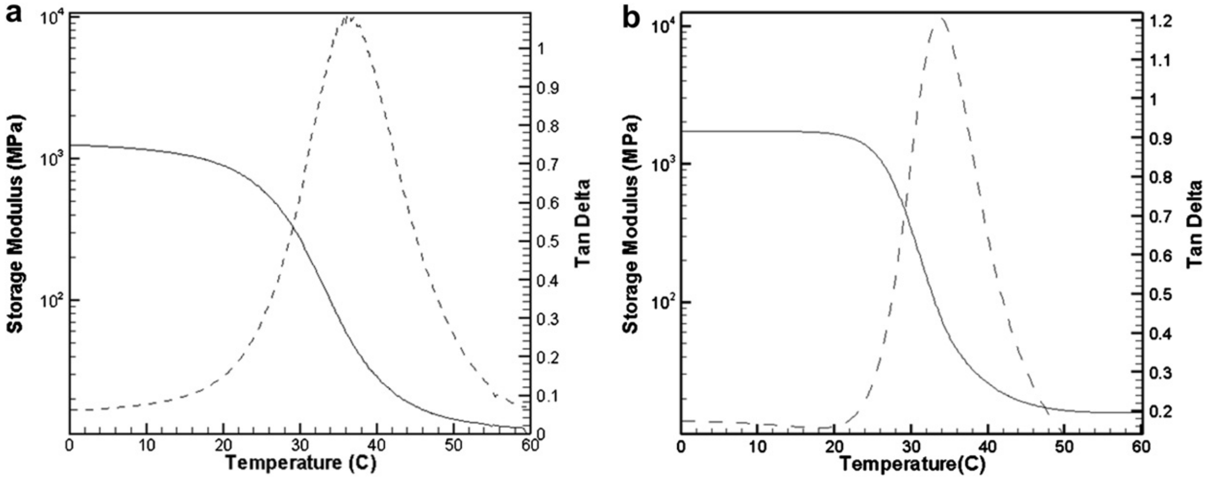


Fig. 4. Storage modulus (–) and tan δ (– –) versus temperature curves for (a) the control shape memory polymer system and (b) the thiol-ene system (TMPTMP/TATATO).

Table 4
Free strain recovery, shape fixity, recovery sharpness, and recovery onset temperature and transition width for each of the shape memory polymer systems.

Formulation	Free strain recovery (%)	Shape fixity (%)	Shape recovery sharpness (%/C)	Strain recovery onset temp (°C)	Strain recovery transition width (°C)
tBA/PEGDMA	96 ± 1	97 ± 2	3.0 ± 0.3	16 ± 4	32 ± 4
TMPTMP/TATATO	96 ± 3	96 ± 3	5.0 ± 0.3	17 ± 1	20 ± 2
IPDUT/APE	97 ± 2	98 ± 2	3.2 ± 1.0	19 ± 3	30 ± 4
IPDUT/IPDU6AE	97 ± 3	97 ± 2	3.0 ± 1.0	17 ± 2	43 ± 4
TMPTMP/IPDU6AE	97 ± 2	97 ± 2	3.1 ± 0.4	13 ± 3	40 ± 3

recovery sharpness of the urethane thiol-ene systems were seen to be around 3%/°C, a value comparable to the acrylic control network and to other documented shape memory systems where other SMPs have been found to exhibit recovery sharpness values that range from 1.8 to 4.2%/°C [9]. The temperature which marked the onset of the free strain recovery of the polymer systems indicates that the shape recovery process for all of the systems began at an average temperature of 16 °C. The onset of shape recovery at a temperature a few degrees below ambient temperature indicates that the polymer would have to be constrained at ambient temperature to maintain its ability to go from its temporary shape to its final shape. This information will impact the storage of these shape memory systems which are designed to activate at body temperature. It has been shown that the onset of strain recovery can be controlled depending on the initial temperature at which the shape memory system was set in its temporary shape [26]. The strain recovery characterization of the thiol-ene systems based on their deformation temperature and subsequent recovery temperature and behavior has not been examined in this paper. Both the thiol-ene and acrylic SMPs exhibited similar and very good strain recovery and shape recovery sharpness.

Constrained stress recovery tests measure the ability of the polymer to reachieve its final shape while being constrained. Constrained stress recovery is the stress generated by the shape memory polymer when acting against an external constraint during heating. The stress exerted by the polymers at T_g demonstrated that all of the polymer systems achieved 100% recovery against the external constraint (Fig. 5).

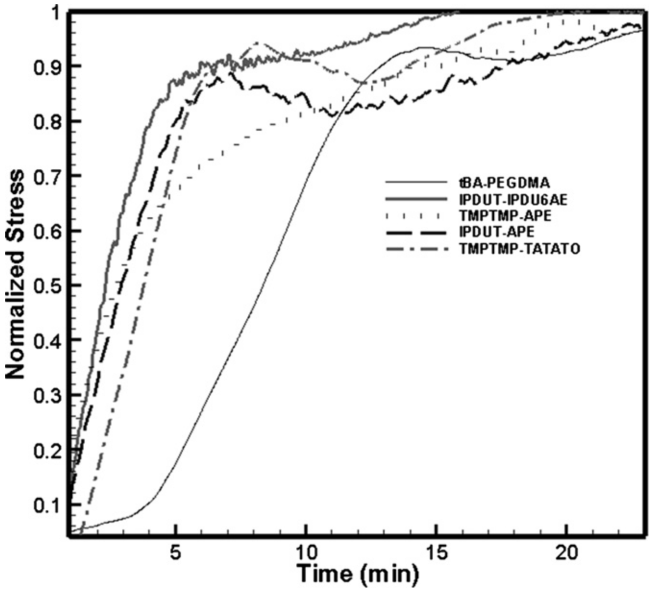


Fig. 5. Constrained stress recovery versus time for the tBA/PEGDMA control system and the thiol-ene systems IPDUT/APE, IPDUT/IPDU6AE, TMPTMP/IPDU6AE and TMPTMP/TATATO.

4. Conclusion

This work demonstrates novel thiol-ene based shape memory polymer systems that can be tailored to exhibit a wide range of polymer mechanical properties suitable for biomedical applications. We have evaluated the shape memory response, thermomechanical, and mechanical properties of the thiol-ene systems in comparison with an acrylic-based shape memory system. Due to the unique thiol-ene step-growth mechanism, thiol-ene polymer systems exhibit a homogeneous network structure. As a result, upon thermal stimulation, the thiol-ene polymer systems exhibit a more rapid and distinct shape memory response as well as improved shape retention as compared to the control system. In comparison to the tBA/PEGDMA control system, the thiol-enes were shown to exhibit comparable elongation, and strain recovery. The thiol-ene system exhibited increased tensile strength, and the urethane thiol-enes exhibited comparable tensile strength to the tBA/PEGDMA control system. The thiol-ene and urethane thiol-ene systems studied in this work demonstrated enhanced toughness and handling characteristics enabling a broader range of device design and manufacturing.

Acknowledgments

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