Body Temperature Triggered Shape-Memory Polymers With High Elastic Energy Storage Capacity

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ABSTRACT: Shape-memory polymers (SMPs) that respond near body temperature are attracting broad interest, especially in the biomedical fields. In this study, the triggering temperature of poly(caprolactone) SMP networks is precisely adjusted by inclusion of non-crystallizable molecular linkers and by variation of prepolymer molecular weight. Longer, non-crystalline linkers and lower molecular weight prepolymers interfere with crystallization, lowering the transition temperature. Networks are prepared with crystallization temperatures that are beneath the human body temperature and yet are above room temperature. Upon cooling such amorphous networks to room temperature, crystallization is sluggish. There, elastomers can be easily strained by several hundred-percent to induce crystallization, thereby fixing strained states. If subsequently heated, programmed SMPs can release significant amounts of stored strain energy (∼3 MJ/m³). SMPs that combine elastic energy storage and exhibit triggering temperatures near the human body temperature could benefit emerging applications in the biomedical space. © 2016 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. 2016, 00, 000–000

KEYWORDS: shape-memory polymers; crystallization; networks; mechanical properties

INTRODUCTION Shape-memory polymers (SMPs) are polymer networks that can be deformed and temporarily fixed into an elastically strained, non-equilibrium shape.1–3 Shape-fixing occurs when strong intermolecular interactions between configurationally distorted polymer chains overcome the chains’ entropic restoring forces. Generally, this is accomplished by cooling an SMP into a crystalline or glassy state or by introducing temporary covalent bonds or non-covalent bonds. Some SMPs can be deformed and fixed in a single step by strain-induced crystallization, obviating the need for a cooling step.4,5 Regardless of how shape-fixing is accomplished, elastic energy is stored until the material is triggered, typically by heating. Then, the material exerts stress and tends toward its equilibrium permanent shape. For a given thermomechanical protocol, SMPs are assessed by their shape-fixity and shape-recovery ratios as well as their volumetric capacity to store elastic energy.6

SMP’s are finding diverse applications, especially the biomedical field. Examples include clot removal devices,7 surgical sutures,8 dialysis needles,9 orthopedic suture anchors10,11 and vascular stents.12 These applications require that the trigger temperature should be near the human body temperature (37 °C). Additional requirements may include: (i) ensuring biocompatibility and sometimes bio-degradability by considering the surrounding biological tissue; (ii) customizing the rate of shape-recovery upon triggering; and (iii) guaranteeing sufficient stored elastic energy density to achieve a shape change against stresses from opposing biological tissue. While several materials meet these needs, precise tuning of the thermal transition temperature remains a challenge. For example, poly(caprolactone)s (PCLs), poly(lactide)s (PLAs), poly(ε-caprolactone)s, and poly(ester urethane)s are often considered, but their thermal transitions are too high (Tm ~ 60, 75 and 45–60 °C respectively).13–15 Several strategies have been attempted to gain control of the shape-memory trigger temperature. For example, the melting of poly(ester urethane)s has been reduced by introducing low molar mass crystallizable soft segments8 and by manipulating the size of phase-segregated hard segment domains.13,15 Another approach to reducing the melting temperature is to create a network polymer with distributed net points. Xu et al. prepared networks from star-shaped PLAs with bulky, rigid nanoparticle POSS cores. The cores reduce entanglements of tethered chains, significantly lowering the...
We recently demonstrated that the elastic energy storage capacity of semicrystalline PCL shape-memory networks can be enhanced by controlling network architecture and chain connectivity. Topologically different networks were prepared from the same batch of three-arm PCL prepolymers. Although networks had the same chemical composition, they differed in chain connectivity. The most “perfect” network was formed by base-catalyzed Michael addition of acrylate-terminated PCL prepolymers with multifunctional thiols. This synthetic approach results in polymer networks that have crosslinks with known functionality, and the molecular weight between crosslinks is predetermined by the molecular weight of prepolymers. Resulting materials are cold-drawable, have good shape-fixity, and a high capacity to store elastic strain energy greater than 1.5 MJ/m³ for fixed strains around 300%.

In the present report, we deliberately design semicrystalline networks with architectures that impede crystallization, effectively depressing crystallization and melting transitions. Base-catalyzed Michael Addition is again employed to form well-defined networks. However, prepolymer chains contain molecular linker groups that are designed to interfere with crystallization. The resulting network is kinetically “frustrated” and can remain in a non-equilibrium, amorphous state for hours. However, amorphous networks at room temperature can be easily programmed by strain-induced crystallization. Heating the strain-crystallized material to temperatures near the body temperature (35 °C) causes crystallites to melt, and material releases its stored elastic strain energy and tends toward its amorphous (crystalline-free) permanent shape. In contrast to prior studies (PEU networks and natural rubber), these deliberately frustrated structures act as rubbery networks with low crystallinity and offer tunability of network melting transition temperatures.

EXPERIMENTAL

Materials

ε-Caprolactone (CL) was purchased from Sigma-Aldrich and distilled before use. All the other chemicals were obtained from Sigma-Aldrich and used as received.

PCL-Triol

The hydroxy-terminated, three-arm PCL was synthesized by ring-opening polymerization (ROP) of CL in the presence of SnOct₂ as a catalyst and trimethylolpropane as a trifunctional initiator. To a dried, silanized 100 mL flask, distilled CL (40.0 g, 39 eq.), trimethylolpropane (1.208 g, 1 eq.) and SnOct₂ (88.8 mg, 1/40 eq.) were added. The reaction was carried out neat, at 120 °C, and under continuous N₂ purge for 24 hours. The resulting PCL polymer was purified by precipitation into methanol followed by vacuum-drying for 12 hours at 60 °C. Yield 92%. The molecular weight was determined by ¹H NMR end-group analysis to be 4,400 g/mol, and the molar mass dispersity from GPC was 1.17. Tri- arm PCL prepolymers with higher molecular weight were obtained using the same technique but with a greater amount of monomer feed.

PCL-Triacrylate

The chain-ends of hydroxyl-terminated prepolymer were acrylated by nucleophilic substitution with acryloyl chloride. To PCL-triol (30.0 g, 1 eq.) under N₂ at 0 °C was added freshly distilled toluene and potassium carbonate (4.23 g, 4.5 eq.). After 30 minutes of degassing with N₂, acryloyl chloride (2.48 mL, 2.78 g, 4.5 eq.) was added dropwise over 15 mins. The reaction was warmed to 80 °C and allowed to stir for 48 hours. The mixture was filtered, and the liquid fraction was precipitated into methanol to afford a white powder. The product, a PCL-triacrylate, was vacuum-dried at 60 °C overnight. Yield 90.0%. ¹H NMR indicated a molecular weight of 5,000 g/mol and complete end-group conversion; GPC showed a molar mass dispersity of 1.18.

PCL-Trithiols

The chain-ends of acrylate-terminated prepolymer were further modified by thiol-acrylate reaction with a dithiol. For example, freshly distilled triethylamine (1 eq.) was added to PCL-triacrylate (10 g, 1 eq.) dissolved in 30 mL of toluene under N₂ purge. A stoichiometric excess of either 1,2-ethanedi- thiol or 2,2’-(ethylenedioxy)diethanethiol (20 eq.) was dissolved in 10 mL of toluene and added dropwise into the reaction flask. The reaction was carried out at room temperature for 24 hours. The mixture was precipitated into methanol to afford a white powder. The product was vacuum-dried at 60 °C overnight. Yield 97.0%. ¹H NMR indicated complete end-group conversion; GPC showed molar mass dispersity of 1.18.

Shape-Memory Networks

Crosslinked films were prepared by thiol-acrylate Michael addition between a PCL prepolymer (PCL-triacrylate or PCL-triol) and a small molecule linker (a dithiol or diacrylate). All thiol-acrylate coupling reactions were conducted in the presence of 4-dimethylaminopyridine (DMAP) (e.g., 1.0 wt %) as a base catalyst. Phenothiazine was added into the mixture as a radical scavenger at 0.5–0.8 wt % to protect the reagent mixture from undue radical-induced polymerization. Stoichiometrically balanced PCL-triacrylate(PCL-3A) and 2,2’-(Ethylenedioxy) diethanethiol (EDDT) afforded network N-L1; balanced PCL-trithiethanol (PCL-3T) and 1,3-butanediol diacrylate afforded N-L2; and balanced PCL-trithioli(PCL-3EOT) and 1,3-butanediol diacrylate afforded N-L3. For each case, the PCL prepolymer and scavenger were first mixed on a glass slide using a spatula, and the mixture was melted on a hotplate at 60 °C. Once a homogeneous mixture was obtained after 1–2 minutes, the difunctional thiol/acrylate was added carefully, and the mixture was melted again for 1–2 minutes. While melted, the finely ground base (DMAP) was added and stirred into the melt for 1–2 minutes. The melted mixture was briefly degassed under vacuum at 60 °C until no bubbles were observed. The mixture was then quickly sandwiched between two glass slides that were
separated by a 0.25 mm thick Teflon spacer. The sandwich was placed in a curing oven (convection) for two days at 60 °C. Samples were dried in a vacuum oven, and gel fraction tests were performed by swelling with acetone followed by drying.

Characterization

$^1$H NMR spectra were acquired on a Bruker AVANCE-III 400 NMR Spectrometer system operating at 400.13 MHz. Molecular weight and polydispersity were measured by gel permeation chromatography (PolyAnalytik PAS103-L and PAS104-L GPC columns and Viscotek TPA301 detector) using THF as an eluent and polystyrene standards. Differential scanning calorimetry was performed using a TA Instrument, Q2000 DSC. Five to six mg samples were placed in a hermetically sealed pan and subjected to heating and cooling at 10 °C/min over the temperature range of −30 to 130 °C. Dynamic Mechanical Analysis (DMA) experiments were performed in tension at 1 Hz and 5 °C/min over the temperature range 25–65 °C using a Rheometrics RSAII solids analyzer. Prepolymer DSC results and network DMA data are available as Supporting Information Figures S1 and S2. Thermo-mechanical analysis was performed using a tensile tester MTS (Q Test/5). All measurements were made on film samples (0.2 mm thickness) that were cut using a trim die according to ASTM D638-Type 5 (gauge length = 7.62 mm). The methodology for strain-induced crystallization and slow-unload shape memory testing is described in the results section. Unless otherwise specified, tensile tests were performed at a strain rate of 30 mm/min. Shape-memory experiments were performed using a custom-made heating chamber.

RESULTS AND DISCUSSION

Network Prepolymers

To introduce non-crystalline linkers into shape-memory networks, PCL prepolymers containing different reactive end-groups were prepared according to Figure 1. Starting from a trimethyloxypropene seed, three-arm, hydroxyl-terminated PCL was grown using ROP of caprolactone. Hydroxyl end-groups were then acrylated to afford a PCL-triacrylate prepolymer, PCL-3A. Subsequent end-group modification by thiol-Michael addition between acrylate ends and dithiols of various sizes achieved PCL-3T and PCL-3EOT. These three sets of were prepared from the same batch of hydroxyl-terminated PCL to isolate the effect of the spacer type on shape-memory properties.

$^1$H-NMR end-group analysis was employed to determine prepolymer MW and to confirm full conversion of end-groups. Signatures of end-group functionality in the NMR spectra...
are also included in Figure 1. Complete substitution of the hydroxyl end-groups after upon acrylation is evident by the disappearance of the resonance peak at $\delta = 3.7$ ppm, corresponding to the adjacent methylene protons. In addition, the simultaneous emergence of acrylate peaks in PCL-3A's spectra between 5.8 and 6.7 ppm confirm substitution. Noticeably, excessive amount of small molecule di-functional thiol ($/C_24_20:1$) is required to fully transform acrylate end-groups into thiols while preventing gelation and preserving the prepolymer’s tri-arm topology. This modification was confirmed by the disappearance of acrylate peaks and emergence of resonances from the ethylene protons of thiol-derived end-groups.

Network Formation

Tri-arm PCL prepolymers were reacted with difunctional small molecules to prepare PCL networks as shown in Figure 2. Curing was conducted at a 1:1 stoichiometric ratio of reactive thiols and acrylate groups to ensure that thermoset networks have a known distribution of molecular weight between crosslinks and a predetermined functionality at each crosslink node. All networks exhibit high gel fractions (> 97%) as reported in Table 1. About 1% of the extracted mass is attributed to unreacted catalyst and free radical scavenger.

The molecular bridge incorporated between PCL chains is referred to as a non-crystalline linker. All linkers were designed to be incompatible with crystalline PCL chains. Since the linkers are relatively short with constrained ends, they are not expected to crystallize. Our hypothesis is that the non-crystalline linkers will interfere with chain crystallization and, therefore, should lower the material’s shape memory transition temperature.

Non-crystalline linkers of various lengths were systematically placed into shape-memory networks using 4, 6, and 8 kg/mol PCL prepolymers. Results are displayed in Table 1. The first three entries have a fixed prepolymer molecular weight and differ only in their type of non-crystalline linker. Networks with a fixed linker type (L1) were also prepared at three different molecular weights. The last two columns of Table 1 display the melting transition temperature and the enthalpy of melting which are discussed in the following section.

Crystallization and Melting

Differential scanning calorimetry (DSC) scans were performed on all crosslinked networks, and Figure 3 displays the second heating scans. The curves each exhibit a mono-disperse, endothermic peak between room temperature and 50 °C, and the
endotherms are attributed to melting of PCL crystalline domains. This melting transition is sensitive to both prepolymer molecular weight as well as the linker size. Compared to their prepolymer counterparts (see Supporting Information Fig. S1), all networks were found to have lower crystallinity and lower melting points. This indicates that crosslinks interfere with the kinetics and the extent of crystallization. Consequently, networks formed from prepolymer with higher molecular weights have a lower density of crosslinks, and therefore exhibit higher melting transition temperatures and larger enthalpies. Networks N4-L1, N6-L1, and N8-L1 form a series with increasing molecular weight between network nodes and display endotherms that peak at 35, 40, and 44 °C, respectively, and exhibit increasing melting enthalpies of 36, 48, and 51 J/g.

The melting transition temperature is also sensitive to the linker type. The linker length was systematically increased in the N4 network series, resulting in lower melting points. The melting temperature of N8 networks was perhaps less affected by the linker type because the non-crystalline linkers are less concentrated.

By adjusting both molecular weight and the linker type, the melting temperature of the well-defined PCL network N4-L2 could be lowered to 30 °C which is in the desired range between room temperature and the human body temperature. It may appear feasible to achieve a network with a similarly low transition temperature (e.g. 30 °C) using a pure PCL network, without non-crystalline linkers, made of low molecular weight prepolymer. However, this approach necessitates a higher crosslink density, compromising the network’s desired shape-memory behavior—e.g., elasticity, shape fixity, and strain-to-break. The advantage of integrating linking groups is the capability of tuning melting transition temperature while preserving the materials’ mechanical properties.

Notably, the network N4-L2, exhibited severely sluggish crystallization at room temperature. Whereas most PCL networks quickly (< 1 min) transform to an opaque, milky white state upon crystallization, N4-L2 remains transparent for a long time (> 10 h) when held at room temperature. The DSC scan shown in Figure 5(b) highlights this difference: no melting transition peak was observed in the specimen that was not drawn, whereas the cold-drawn sample exhibits a melting endotherm.

A qualitative shape-memory test was performed to demonstrate the utility of adjusting the shape-memory triggering temperature to near body temperature. A small specimen from a network film N4-L2 was folded and cooled with ice. The sample remained folded even when it was warmed to room temperature. The folded region was briefly contacted (< 10 s) by a human finger, and the folded specimen immediately reverted to its original, unfolded state. A time-lapse image is shown in Figure 4. A video illustrating cold-drawing and body temperature triggering is available as Supporting Information. The following sections will focus on the unique shape-memory characteristics of the N4-L network.

### Table 1: Composition, Calorimetry Results, and Gel Fraction of Prepared Shape-Memory Networks

<table>
<thead>
<tr>
<th>Network</th>
<th>Prepolymer</th>
<th>Non-crystalline Linker</th>
<th>Prepolymer MW (Da)</th>
<th>Prepolymer PDI</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Gel Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>N4-L1</td>
<td>PCL-3A</td>
<td>EDDT</td>
<td>4,400</td>
<td>1.18</td>
<td>35.07</td>
<td>35.84</td>
<td>98.5%</td>
</tr>
<tr>
<td>N4-L2</td>
<td>PCL-3T</td>
<td>BDDA</td>
<td>4,400</td>
<td>1.18</td>
<td>32.24</td>
<td>34.65</td>
<td>98.2%</td>
</tr>
<tr>
<td>N4-L3</td>
<td>PCL-3EOT</td>
<td>BDDA</td>
<td>4,400</td>
<td>1.18</td>
<td>30.88</td>
<td>34.65</td>
<td>98.7%</td>
</tr>
<tr>
<td>N6-L1</td>
<td>PCL-3A</td>
<td>EDDT</td>
<td>6,200</td>
<td>1.20</td>
<td>39.98</td>
<td>48.41</td>
<td>99.0%</td>
</tr>
<tr>
<td>N8-L1</td>
<td>PCL-3A</td>
<td>EDDT</td>
<td>8,100</td>
<td>1.14</td>
<td>42.78</td>
<td>50.06</td>
<td>97.8%</td>
</tr>
<tr>
<td>N8-L2</td>
<td>PCL-3T</td>
<td>BDDA</td>
<td>8,100</td>
<td>1.14</td>
<td>44.08</td>
<td>50.97</td>
<td>98.2%</td>
</tr>
</tbody>
</table>

* BDDA: 1,3-butanediol diacrylate; EDDT: 2,2’-(Ethylenedioxy)diethanethiol.
* Determined from 1H-NMR.
* Determined from GPC.
If a semicrystalline polymer is melted and strained while in the amorphous state, not far from its crystallization temperature, the entropy loss of polymer chains can cause strain-induced crystallization. Formed crystals then exhibit melting points that exceed the temperature at which the sample was drawn, leading to stabilization of the deformed state. Network N4-L2 was melted and cooled to room temperature, where it appears non-crystalline, and can be easily strained to form crystals that are stable at room temperature. For example, a sample was melted at 42°C and then cooled to 25°C where it remained transparent for over 1 hour, suggesting a state with little crystallinity. Then, upon drawing N4-L2 at room temperature to 200% strain, the specimen quickly (<30 s) transformed into a semi-transparent state. Figure 5 shows images before and after strain induced crystallization of N4-L2—the sample opacity changes from transparent to milky-white, indicative of crystallite formation. DSC experiments of material harvested from the cold-drawn specimen show clear melting endotherms [Fig. 5(b)], confirming the explanation. This phenomenon was also well understood through small-angle X-ray scattering (SAXS) in a few previous reports.21–23

Another N4-L2 specimen was subjected to a slow-unload shape-memory method to assess shape-fixity and the material’s ability to store elastic energy. The test protocol is outlined in Figure 6 and includes the following steps: (i) at room temperature, the sample is drawn 15mm/min to 400% of its initial gauge length; (ii) the sample is held at 400% strain for five minutes; (iii) the tensile load is removed and the sample is allowed to elastically recover to its fixed strain; (iv) at constant strain, the sample is heated to 42°C, causing stress to develop; (v) the sample is further held at constant strain for at least 120 seconds, or until the stress finally ceases to change; (vi) last, the sample is slowly unloaded at a constant rate of 0.5 MPa/min, allowing the sample to perform measurable work as it retracts. The unload rate is performed slowly to maintain equilibrium stress at each differential strain state during shape recovery. The work is calculated by integration of the raw force-distance data obtained during the final step. Upon reaching a zero-stress condition, the crosshead gauge length was returned to its original zero-stress value, and the sample was allowed to fully recover to its permanent shape. The sample was allowed to crystallize at room temperature for 20 min before starting the subsequent cycle.

Five successive slow-unload cycles of N4-L2 are displayed in Figure 6(b). The first slow-unload cycle showed higher fixity than the following four cycles, and this is attributed to shape-training effect where the state of crystallization during the first cold-drawing may differ that of the higher cycles.'
Cycle 2 to 5 appeared nearly identical, with a shape-fixity of about 86% and full recovery upon heating. During each cycle, when heat is applied under a fixed strain condition, the generated stress peaked at nearly 2.0 MPa, which is among the highest value observed in similar PCL networks. Noticeably, the slow-unload curve generated at 42 °C exceeds the original cold-draw stress curve generated at room temperature. This is attributed to greater entropic elasticity that is present at elevated temperatures.

The elastic energy storage capacity of each cycle was calculated by integrating the stress vs. strain curves from the slow-unload phase (see Supporting Information). The energy efficiency of each cycle was then determined by computing the ratio of the work recovered during the slow-unload step to the work input during cold-drawing. The measured energy density of N4-L2 during recovery from a cycle with 400% initial strain was 3.26 MJ/m³, corresponding to an efficiency of 85%. These values are among the highest reported for SMPs that are fixed at around 300-400% strain. The efficiency is remarkable as well—PCL networks in our prior study exhibited values below 20% because, during cold-drawing, much energy is expended to disrupt and reorient crystals present at room temperature. N4-L2’s resistance to crystallization at room temperature enables the sample to be easily cold-drawn, improving the cycle efficiency. If N4-L2 were allowed to crystallize for several hours, more work would be required to strain the sample, and this would lower the sample’s shape memory efficiency.

Network N4-L2 was further stretched to different elongations to determine how shape-fixity depends on strain. The same slow-unload method described above was followed, only with different initial strain percentages. The results, also shown in Figure 6, indicate that fixity is improved with deformation to higher strain. When samples are deformed to smaller strain (e.g., ~100%), strain-induced crystals were too few or too weak to stabilize the elastic deformation. With greater strain, stretched network strands have a greater tendency to form more stable and highly oriented crystallites. The fifth cycle was deformed to 600% strain and the sample failed during the slow-unload step. The strain dependence can be viewed as indication of a proper working strain range for such materials.

The shape-memory properties of networks N6-L1 and N8-L2 are also summarized in Table 2. These networks are derived...
from prepolymers with longer molecular weights, and, therefore, are somewhat softer and have higher crystallinity at room temperature. Consequently, these materials exhibit lower elastic energy storage for the prescribed shape-memory test at 400% strain.

CONCLUSIONS

In summary, we examined how the crystallization temperature of model PCL networks is sensitive to (i) the type and density of molecular linker groups and (ii) the prepolymer molecular weight. Optimized shape-memory networks are frustrated and crystallize sluggishly when cooled to room temperature. Moreover, when stretched to a relatively small strain of 400%, networks exhibit strain-induced crystallization, leading to high strain fixity (~90%) and high elastic energy storage density (~3.0 MPa/m^3). Thermomechanical shape-memory tests showed the majority of strain-energy used to program a material (>80%) could be stored and recovered upon subsequent shape-triggering. Unlike other PCL networks that require energy to be expended to disrupt and reorient crystals during cold drawing, N4-L2’s resistance to crystallization at room temperature enables the sample to be easily cold-drawn.

Generally, SMPs with crystallization temperatures between room temperature and the human body temperature are ideal for a variety of applications, especially in the biomedical fields. The material may be used in medical devices where thermally-induced stress accumulation or the attainment of physical work is desired. Examples may include sutures, artificial skin, body-heat assisted medical or consumable dispensers, and so on.

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