Shape memory poly(ε-caprolactone)-co-poly(ethylene glycol) foams with body temperature triggering and two-way actuation†

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Electronic Supplementary Information (ESI)

Supplemental Method 1: PCL Functionalization through End-Capping
To enable crosslinking through thiol-ene chemistry, PCL diol was end-capped with acryloyl chloride (Figure S1). PCL diol with a Mn of 3,000 g/mol (Scientific Polymer) was dissolved in anhydrous benzene (Sigma) at room temperature under nitrogen purge. After the PCL was completely dissolved, triethylamine (Sigma) was added in a 2.5 times molar ratio to PCL. Acryloyl chloride at 2.5 times the molar ratio of PCL was then added dropwise, and the reaction was carried out at 80 °C for 3 h under nitrogen purge. The salt products were filtered and the end-capped PCL precipitated in cold hexanes.

Figure S1: PCL End-Capping Chemistry
Supplemental Method 2: PEG Functionalization through End-Capping

PEG was end-capped with allyl diisocyanate (Figure S2) to enable crosslinking via thiol-ene chemistry. PEG diol with a Mn of 4,000 g/mol (Scientific Polymer) was dissolved in distilled toluene at 60 °C under nitrogen purge. Two drops of dibutyltin dilaurate (Sigma) was added to the solution for catalysis. Allyl isocyanate was added dropwise to the solution at 2.5x the molar ratio of PEG. The reaction was carried out at 90 °C for 4 h, followed by precipitation in cold hexanes.

Figure S2: PEG End-Capping Chemistry

\[
\begin{align*}
\text{PEG Diol} & \quad + \quad \text{allyl isocyanate} \\
\text{Dibutyltin Dilaurate} & \quad \rightarrow \\
\text{Anhydrous Toluene} & \quad 4 \text{ h} \quad 90 \, ^\circ \text{C} \\
\text{PEG Diallyl Acrylamide} & \quad 
\end{align*}
\]
Supplemental Method 3: Salt Fusion Process
To improve pore interconnectivity, salt was fused prior to polymer synthesis. For this study, 2.5 g of salt with 150-300 µm diameter was added to a 20 mL glass vial. The glass vial was placed in a Styrofoam box (9.25 x 6.25 x 8.25 in) with the lid off. A 2 L beaker with 2 L of water at approximately 37 °C (hot water from faucet) was placed in the Styrofoam box. The box was closed and after 24 h the vials were removed and the salt had fused.

Supplemental Method 4: Example PCL-co-PEG synthesis
Foam scaffold synthesis was carried out in a 20 mL glass vial containing fused salt (see Supplemental Method 3). All foams were fabricated using a 9:1 salt:polymer ratio by weight. For an 80PCL-20PEG sample with 2.5 g of salt, the following protocol was used: 222 mg of functionalized PCL and 55.6 mg of functionalized PEG were added to a 20 mL glass vial. Added to that same vial was 202 µL of tetrathiol dissolved in dichloromethane (0.1 g of tetrathiol per mL of DCM) yielding a molar ratio of 2:1 polymer:tetrathiol. Next, 2.8 mg of DMPA photoinitiator was added. Extra DCM was added to bring the total solution volume to 625 µL. After mixing, the solution was added dropwise to the fused salt and UV cured for 2 h (Black Ray, 365nm, 2.0 mW/cm²). Following curing, samples were dried in vacuum overnight. Salt was extracted by adding water to each vial and placing in a shaker at 37 °C for 48 h. Samples were then dried prior to characterization.

Supplemental Method 5: Microtomography
For microtomography characterization, 10.2 mm diameter and 3 mm thick discs were used. A Scanco Medical µCT40 scanner was used. Samples were placed in a 12 mm diameter sample tube and scanned with a voltage of 45 kV and 177 µA. Scanning parameters led to a nominal voxel resolution of 12 µm. From the reconstructed slices of 5 foam samples prepared with 150-300 µm diameter fused salt, a porosity of 79 ± 5 % was obtained.

Supplemental Method 6: One-Way Shape Memory
One-way shape memory testing was performed in a dynamic mechanical analyzer (TA Q800) using compression platens. Circular discs of 7 mm diameter and 3 mm thickness were tested. Using the force controlled method in the Q800, a preload force of 0.01 N was applied. Samples were heated to 80 °C and loaded with a force rate of 0.5 N/min until reaching the force limit of the Q800 of 18 N. Samples were then cooled at a rate of 3 °C/min to -10 °C and held isothermal for 5 min for crystallization. The sample was then unloaded at a rate of 0.5 N/min to the preload force of 0.01 N to observe fixation. Samples were then heated at 3 °C/min to 80 °C to observe recovery.

Supplemental Method 7: Differential Scanning Calorimetry
To determine the melt transition temperatures of the different compositions, a TA Q2000 differential scanning calorimeter was used. Samples ranging from 3-6 mg were placed in Tzero aluminum pans (TA Instruments). First, samples were equilibrated to 80 °C and held isothermal for 1 min. Next samples were cooled at 3 °C/min to -10 °C and held isothermal for 1 min. Samples were next heated at 3 °C/min to 90 °C. Melting transition temperatures were determined.
from the exothermic peak of this second heating cycle and crystallization temperatures determined from the endothermic peak from the cooling cycle (Figure S3). Hydrated samples were soaked in water for 24 h prior to performing differential scanning calorimetry. These samples had larger masses as they contained water, and the same protocol was used to determine the hydrated melting transition temperature.

**Figure S3: Composition Effect on Melting Transition.** (a) 2nd heat and 1st cooling cycles for dry foams for different compositions of PCL-PEG. (b) 2nd heat and 1st cooling cycles for hydrated foams for different compositions of PCL-PEG.

**Figure S4: Composition Effect on Melting Transition.** (a) 2nd heat and 1st cooling cycles for dry films for different compositions of PCL-PEG. (b) 2nd heat and 1st cooling cycles for hydrated films for different compositions of PCL-PEG.
Supplemental Method 8: Varying Deformation Temperature

Deformation temperature studies were conducted in a TA Q800 dynamic mechanical analyzer. Circular discs of 7 mm diameter and 3 mm thickness were used in the compression platens of the TA Q800. For each run, thermal history of the sample was removed by equilibrating to 80 °C, holding isothermal for 5 min, cooling to -10 °C at a rate of 3 °C/min and holding isothermal for 5 min. This allowed the same crystallization kinetics to occur for testing at each deformation temperature. Next, samples were heated at 3 °C/min to a specified deformation temperature (Tm-5, Tm, Tm+5, and Tm+10) and deformed at 0.5 N/min until reaching 30% strain. While holding the stress constant, samples were then cooled at 3 °C/min to -10 °C and held isothermal for 5 min to allow crystallization. Samples were then unloaded at 0.5 N/min to the preload force of 0.01 N to observe shape fixing. After unloading, samples were heated at 3 °C/min to 27 °C and held isothermal at that temperature for 20 min. This step allowed for determination of the stability of the fixed shape at room temperature. Samples were then heated at 3°C/min to 80 °C to observe the recovery profile and percent recovery of the samples. Stress-temperature-strain plots for each deformation temperature reveal a decrease in the onset of recovery temperature as deformation temperature decreases (Figure S5).

Figure S5: Deformation Temperature Effect on Shape Memory. Shape memory plots for deformations of i) Tm + 30 °C, ii) Tm + 10 °C, iii) Tm, iv) Tm – 5 °C, v) Tm – 10 °C, and vi) Tm – 15 °C, reveal a decrease in the onset of recovery as deformation temperature decreases, and a decrease in fixing when deforming below Tm.
Supplemental Method 9: Determining the Effect of Compressive Strain on Recovery
For the temperature deformation studies, an earlier onset of recovery was observed when
deforming at lower temperatures. To determine if this effect was due to “temperature memory”
or due to a difference in heat flux caused by the different strains induced into the foams at the
lower temperatures, a foam sample was deformed, at the same temperature, to different strains
and the recovery profile analyzed. A foam sample was subjected to a one-way shape memory test
following the sample protocol in Supplemental Method 6, with the exception of loading to
predetermined strains of 20, 40 and 60%. The results show that the amount of compressive strain
had a negligible effect on the onset recovery temperature (Figure S6).

Figure S6: Compressive Strain Influence on Recovery. Recovery traces of an 80PCL-
20PEG foam was deformed at 80 °C to strains of 20, 40 and 60% and subjected to one-way
shape memory reveal no difference in recovery onset.

Supplemental Method 10: Two-Way Shape Memory
Two-way, reversible shape memory testing for samples in compression was carried out using the
TA Q800 dynamic mechanical analyzer. Discs of 7 mm diameter and 3 mm thickness were
tested in the compression platens of the Q800. Samples were equilibrated to 80 °C and held
isothermal for 2 min. Samples were loaded at 0.5 N/min until reaching a predetermined strain
(10, 20, 30, 40, 50, or 60%) and then cooled at 3 °C/min to -20 °C while the stress was held
constant and held isothermal at that temperature for 5 min. During the cooling and isothermal
step at -20 °C, samples experienced stress-induced compression. While holding the stress
constant, samples were then heated at 3 °C/min to 80 °C, where samples recovered the stress-
induced compression. Two-way shape memory of solid cylinders were also performed (Figure
S7).
Figure S7: Two-Way Shape Memory of Solid Cylinder. Two-way shape memory of solid 80PCL-20PEG cylinders in compression reveal the solid architecture is capable of two-way actuation, but actuation strains are much lower than were observed in comparable foams. Here two strains were used for the initial deformation, 30% and 36% (which reached the force limit of the DMA). Actuation strains of ~7% were achieved.

Supplemental Method 11: Water Uptake

Water uptake experiments were conducted on foams and films with various PCL-PEG compositions (Figure S4, Table S1). Foam samples ranging from 13-34 mg in weight and film samples ranging from 82-148 mg were soaked in room temperature water for 24 h. Surfaces of the samples were dried with a kimwipe and the mass of each sample weighed. Water uptake was defined as the ratio of the wet weight to dry weight. With increasing PEG composition, both the films and the foams showed increasing water uptake percent. Foams consistently had a higher water uptake due to water filling in the pores and not just swelling the polymer (Figure S8).
Figure S8: Water Uptake Increases with Increasing PEG composition.

Table S1: Raw Mass Measurements for Foams Before and After Hydrating

<table>
<thead>
<tr>
<th>Composition (Foam)</th>
<th>Dry Weight (mg)</th>
<th>Wet Weight (mg)</th>
<th>Water Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100PCL-0PEG</td>
<td>34.6</td>
<td>60.2</td>
<td>73.9</td>
</tr>
<tr>
<td>90PCL-10PEG</td>
<td>16.5</td>
<td>37.8</td>
<td>128.7</td>
</tr>
<tr>
<td>80PCL-20PEG</td>
<td>14.4</td>
<td>31.2</td>
<td>116.6</td>
</tr>
<tr>
<td>70PCL-30PEG</td>
<td>18.1</td>
<td>48.8</td>
<td>169.8</td>
</tr>
<tr>
<td>60PCL-40PEG</td>
<td>23.6</td>
<td>62.3</td>
<td>164.0</td>
</tr>
</tbody>
</table>
Supplemental Movie
Here an 80PCL-20PEG sample with a hydrated Tm of 36 °C is triggered to expand in water at a temperature of 37.6 °C. Prior to the addition of the water, the scaffold was heated to 80 °C, compressed between two steel plates, and fixed in a -4 °C freezer for 10 min.