Synthesis and Characterization of a New Class of Shape Memory Polymers for Development of "Smart" Vascular Constructs

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Introduction – Shape Memory Polymers

- Shape memory polymers (SMPs) are materials that can be molded into different shapes but will also return to their original shape with a specific stimulus
- Our aim is to create an injectable thermal responsive SMP based on poly(caprolactone) (PCL)-derived copolymers that can be used for implantable vascular patches
- PCL's biodegradability and biocompatibility make it a promising base for SMPs

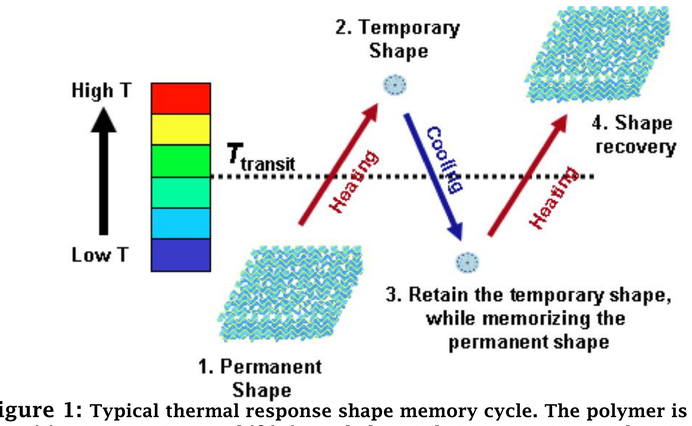


Figure 1: Typical thermal response shape memory cycle. The polymer is heated past a transition temperature and if it is cooled past that temperature under strain, it keeps that temporary shape until it is reheated. Diagram Courtesy of Dr. Hak-Joon Sung

Polymer Synthesis

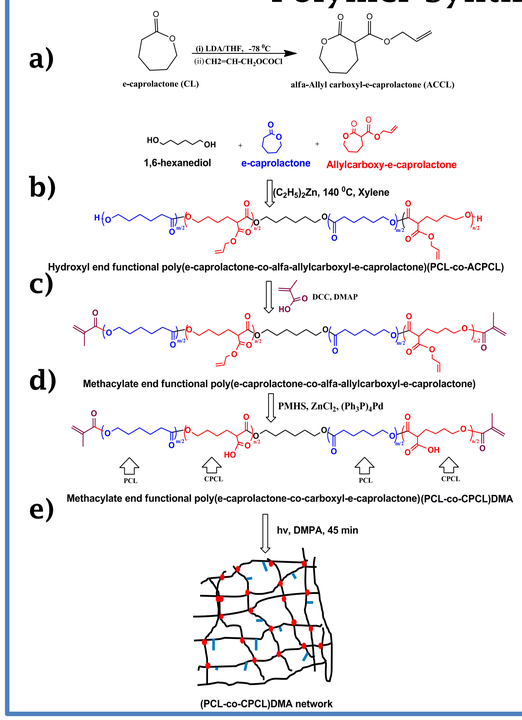


Figure 2: Our synthesis scheme. **a)**, α-(allyloxycarbonyl)-ε-caprolactone (ACCL) is synthesized to be used as a monomer. **b)** We polymerize 1,6-hexanediol with ε-caprolactone and ACCL with diethyl zinc as a catalyst to get PCL-ACPCL. **c)** The polymer ends are functionalized with methacrylate groups which allow the polymer to crosslink. **d)** The carboxyl groups inside the chain are deprotected by removing the allyl groups. These carboxyl groups are to be used for peptide linkage in the future. **e)** We crosslink the polymer under ultraviolet radiation in a solution of methylene chloride by using 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) as a photoinitiator.

Characterization of Shape Memory Polymer

Differential Scanning Calorimetry (DSC)

- DSC measures heat flow associated with phase changes as a function of temperature.
- We use it to determine the melting (transition) and crystallization temperatures as well as the glass transition point.

Dynamic Mechanical Analysis (DMA)

- In DMA, the polymer is characterized as it is subjected against different forces, deformations, and temperatures.

Contact Angle Characterization

- Water is dropped on the polymer film and the contact angle is recorded using a goniometer
- The way the water wets across the surface gives us an idea of the film's hydrophilicity

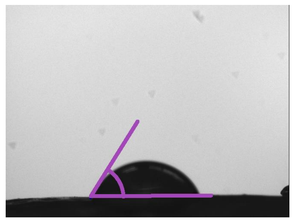


Figure 3 (Left): A picutre of a 26%ACPCL-74%PCL film on the goniometer. The goniometer measures the angle at which a drop of water lays on the film. Picture courtesy of Joshua Stewart

Figure 4 (Right): A typical DSC graph after the thermal history has been removed. The exothermic peaks (pointing upward) represent crystallization peaks and the endothermic peaks (pointing downward) represent transition peaks. The curve at ~-50 represents a glass transition state

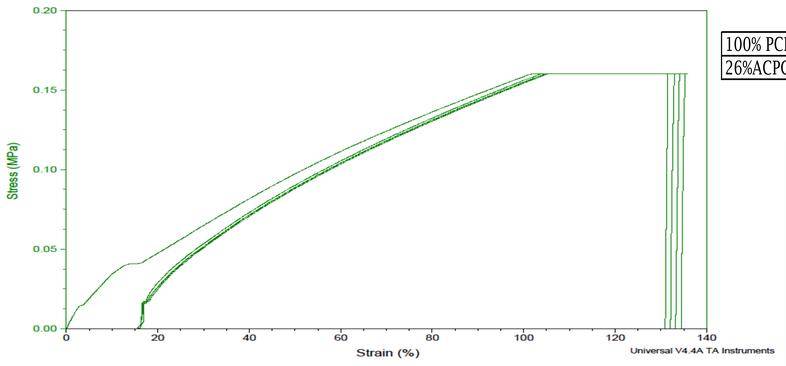


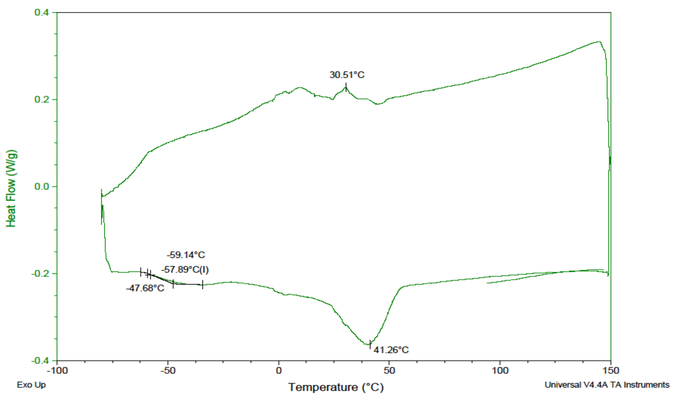
Figure 5 (Bottom): A DMA plot of a 100% PCL during a thermomechanical cycle experiment. The stress and strain are measured as the temperature and force are cycled between 10-60˚C and 0.005-0.5N.

Table 1 (Right): Preliminary data for two films. We see that hydrophilicity, transition temperature, and crystallinity decrease as the amount of PCL decreases

	DSC Data					Goniometer Data			
	Glass Transition Point (°C)	Crystallization Point (°C)	Melting (Transition) Point (°C)	Enthalpy of Crystallization (J/g)	Enthalpy of Fusion (J/g)	Right Contact Angle (°)	Left Contact Angle (°)	Width of Droplet (mm)	Height of Droplet (mm)
100% PCL	N/A	26.44	49.11	37.22	38.08	46.8	48.4	3.675	0.627
26%ACPCL-74%PCL	-58.91	29.90	38.65	1.36	17.78	71.8	70.7	2.654	0.801

Preliminary Results

- Our synthesis is capable of producing polymer films that have transition temperatures around body temperature (~29-41) and have molecular weights of 10 kDa although the weights are not consistent
- The polymer films yield under 1 N of force applied
- The films exhibit slightly different thermal properties once their thermal histories have been destroyed. Prior to this, most exhibited multiple transition and crystallization peaks due to heterogeneity.



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Conclusions and Future Work

- We have seen that we can make polymer films that transition at the appropriate temperature
- Testing has shown that most of the films we've made cannot withstand much force (<1 N)
- Run Gel Permeation Chromatography (GPC) to estimate the molecular weight and degradation time of the polymers based on their elution times compared to standards.
- Enhancing the reproducibility of the synthesis & crosslinking to get consistent molecular weight, thermal properties, and mechanical properties.
- Tune the molar concentrations of PCL & ACPCL in order to create a film with an appropriate transition temperature as well as one that can withstand appropriate force
- Continue thermomehcanical cycle experiments to calculate and optimize shape fixity and strain recovery rate.