Supporting Information

Gold Nanorods or Nanospheres? Role of Particle Shape on Tuning the Shape Memory Effect of Semicrystalline Poly(ε-caprolactone) Networks

Haikun Xu and Bridgette M. Budhlall*

Department of Plastics Engineering and Nanomanufacturing Center, University of Massachusetts, Lowell MA. 01854, USA

Contents:

1H NMR spectrum of step I monomer (3-Phenyl-acrylic Acid 4-hydroxyl-cyclohexyl Ester) (Figure S1)................................................................................................................................S2

1H NMR spectrum of step II monomer (3-Phenyl-acrylic Acid 4-Oxocyclohexyl Ester) (Figure S2)................................................................................................................................S2

1H NMR spectrum of step III monomer (3-Phenyl Acrylic Acid 4-Oxo-oxepan-4-yl Ester) (Figure S3)........................................................................................................................................S3

1H NMR spectrum of PCL modified tri-block copolymer (homo-block) (Figure S4)...........S3

TGA curve for the SMP without AuNPs (Figure S5).............................................................S4

TGA curve for SMP/AuNS (0.2wt%) composite (Figure S6)..................................................S4

TGA curve for SMP/AuNR (0.2wt%) composite (Figure S7).................................................S5

TEM images of SMP/AuNRs sample and the gold nanorods (Figure S8)....................S6

SEM images of SMP/AuNR samples with EDS spectrum (Figure S9).............................S7

Photograph of the self-customized UV-crosslinking set-up (Figure S10).....................S8

Photograph of uniformly dispersed AuNS and AuNR in the SMP acetone solution (Figure S11)........................................................................................................................................S8

Photograph of uniformly dispersed AuNR and AuNS in the SMP film made in a Teflon mold (Figure S12).....................................................................................................................................S9

Cyclic, thermomechanical experiments for crosslinked SMP (Figure S13)......................S9

Aspect Ratio, Concentrations and SPR Peak Wavelength of AuNPs in SMP (Table S1)....S10

Description of a time-continuous movie showing IR laser-triggered shape recovery tests for the SMP/AuNR nanocomposite films (Movie M1)......................................................................................................................................S10
Figure S1. $^1$H NMR spectrum of step I monomer (3-Phenyl-acrylic Acid 4-hydroxyl-cyclohexyl Ester).

Figure S2. $^1$H NMR spectrum of step II monomer (3-Phenyl-acrylic Acid 4-Oxocyclohexyl Ester).
**Figure S3.** $^1$H NMR spectrum of step III monomer (3-Phenyl Acrylic Acid 4-Oxo-oxepan-4-yl Ester).

**Figure S4.** $^1$H NMR spectrum of PCL modified tri-block copolymer (homo-block).
Figure S5. TGA curve for the SMP without AuNPs.

Figure S6. TGA curve for SMP/AuNS (0.2wt%) composite.
Figure S7. TGA curve for SMP/AuNR (0.2wt%) composite.
Figure S8. TEM images of gold nanorods (a-c) after incorporation into the SMP nanocomposites at 0.2 wt% loading and, (d) before incorporation into the SMP. The nanorods exhibited an aspect ratio of ~4, with an average length and width of $40 \pm 5$ nm and $10 \pm 2$ nm respectively, in both samples. The TEM images in (a-c) are shown at the same magnification.
**Figure S9.** SEM images of the SMP/AuNR sample with EDS spectrum taken at the cluster of rod-shaped structure (marked by ○). Many individual AuNRs are highlighted with ○
**Figure S10.** Photograph of the self-customized UV-crosslinking setup.

**Figure S11.** Photograph of uniformly dispersed AuNS (left) and AuNR (right) in the SMP solution in acetone.
Figure S12. Photograph of uniformly dispersed AuNR (left) and AuNS (right) in the SMP film in a Teflon mold.

Figure S13. DMA curve of thermos-mechanical test for the shape memory polymer. The shape programming and shape recovery procedures are shown in the curve. This is the first thermo-mechanical shape memory cycle. The shape fixity ratio ($R_f$) and shape recovery ratio ($R_r$) were calculated to be 98.7% and 84.6%, respectively.
Table S1. Aspect Ratio, Concentrations and SPR Peak Wavelength of AuNPs in SMP

<table>
<thead>
<tr>
<th>Nanocomposite Sample</th>
<th>Size of AuNP (nm)</th>
<th>Concentration of AuNP (wt %)</th>
<th>SPR Peak Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMP/AuNR</td>
<td>Diameter: 10</td>
<td>0.10</td>
<td>808</td>
</tr>
<tr>
<td></td>
<td>Length: 41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Aspect ratio: 4.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMP/AuNR</td>
<td></td>
<td>0.20</td>
<td>808</td>
</tr>
<tr>
<td>SMP/AuNS</td>
<td>Diameter: 20</td>
<td>0.20</td>
<td>520</td>
</tr>
</tbody>
</table>

**Movie S1:** A visual demonstration of IR laser-triggered shape recovery tests was video-recorded at a rate of 60 fps. In the first half of the movie, the AuNR/SMP nanocomposite film recovered to a permanent coil upon radiation of the IR laser. The second half of the movie demonstrated the reversed process of converting to a flat strip from a AuNR/SMP nanocomposite coil shape.