

# Dynamic Optical Gratings Accessed by Reversible Shape Memory

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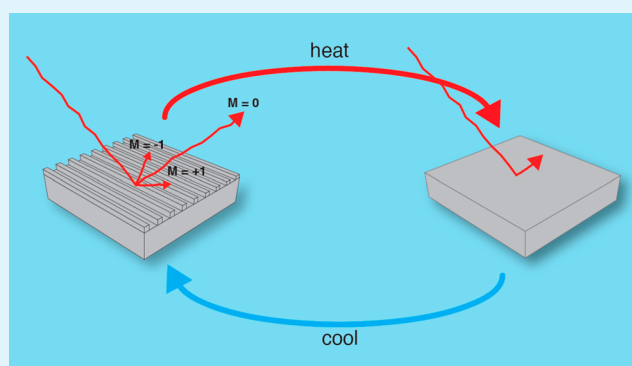
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## Supporting Information

**ABSTRACT:** Shape memory polymers (SMPs) have been shown to accurately replicate photonic structures that produce tunable optical responses, but in practice, these responses are limited by the irreversibility of conventional shape memory processes. Here, we report the intensity modulation of a diffraction grating utilizing two-way reversible shape changes. Reversible shifting of the grating height was accomplished through partial melting and recrystallization of semicrystalline poly(octylene adipate). The concurrent variations of the grating shape and diffraction intensity were monitored via atomic force microscopy and first order diffraction measurements, respectively. A maximum reversibility of the diffraction intensity of 36% was repeatable over multiple cycles. To that end, the reversible shape memory process is shown to broaden the functionality of SMP-based optical devices.

**KEYWORDS:** shape memory polymers, reversible shape memory, responsive surfaces, photonic structures, elastomers



## INTRODUCTION

Technological advances increasingly require optical components to be adaptable and multifunctional. Standard photonic components are typically crafted from rigid materials, with photonic structures often fabricated using ruling processes and copied with other rigid materials.<sup>1</sup> This rigidity allows photonic components to have only a single designed function, while in some cases, switchable micro-optics components are desirable. Advances in soft lithography have allowed for the production of adaptable optical elements that use polydimethylsiloxane (PDMS) elastomers to mold photonic shapes.<sup>2–5</sup> These photonic replicas can be stretched or compressed to induce a tunable optical response and thus have shown a promising ability for use in optical setups, but the need for constant loads to be applied limits the application of these devices.

Shape memory polymers (SMPs) are polymer networks capable of switching from one programmed shape to another. Two programming steps are necessary to prepare a semicrystalline elastomer for shape memory actuation. First, an original (primary) shape is obtained via physical or chemical cross-linking.<sup>6</sup> The temporary (secondary) shape is then programmed by heating the cross-linked sample above its melting temperature ( $T_m$ ), applying a force, and cooling below  $T_m$  with the force still in place. When the force is removed, the secondary shape is maintained until a suitable external stimulus of heat, sound, light, or electricity is applied.<sup>7–10</sup> However,

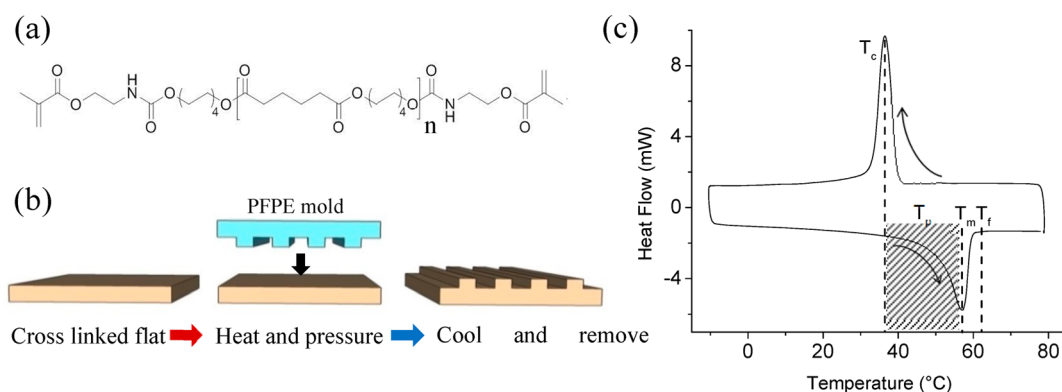
without external forces or designed structural constraints, most shape memory processes are irreversible.<sup>11–13</sup> Recent studies have shown that it is possible to reversibly “shape-shift” between two programmable shapes without applying external forces or reprogramming in a process called reversible shape memory (RSM). This approach offers a new route to hands-free multifunctionality<sup>14–16</sup> and is a consequence of the interplay of the crystalline scaffold and chemical cross-links, which are each capable of encoding a distinct shape. Partial melting of the crystalline scaffold leaves behind a latent crystalline template, and the programmed shape is recovered upon cooling by self-seeded crystallization along kinetically preferred pathways to replicate the scaffold. The reversibility is controlled by tuning the chemical cross-linking density and the partial melting temperature. At a macroscopic scale, the maximum reversibility of tensile strain has been reported as 75% for poly(octylene adipate) elastomers.<sup>14</sup>

Compared to rigid optical components, SMP optics can be tunable with no external force needed to maintain a secondary shape. At smaller scales, SMPs have been explored for their ability to memorize micrometer and sub- $\mu\text{m}$  features as well.<sup>17–19</sup> For example, Xu et al. crafted deformable micro-

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**Figure 1.** (a) Chemical structure of methacrylate-terminated poly(octylene adipate) ( $n = 13$ ). (b) The molding process: a glass slide is used to cure an optically flat surface of poly(octylene adipate). A 750 nm pitch perfluoropolyether (PFPE) grating is used as a mold to emboss the heated flat surface. After cooling, the mold is removed, and the grating structure remains on the SMP surface. (c) A differential scanning calorimetry (DSC) thermogram of a cross-linked POA sample indicates the temperature range of partial melting temperatures ( $T_p$ , hatched region), the melting peak ( $T_m = 58$  °C), the temperature of complete melting ( $T_f = 64$  °C), and the crystallization peak ( $T_c = 37$  °C) (arrows indicate ramping direction).

optic surface structures from SMPs for use as dynamic optical components.<sup>17</sup> However, the advantages of SMP micro-optics are often hampered by the irreversibility of most shape memory processes. Previous studies have demonstrated that micro-structured surfaces can be modulated via RSM to change surface effects including adhesion and wetting.<sup>18</sup>

Here, we report on the utilization of RSM at a sub- $\mu\text{m}$  scale to create a reversibly tunable optical element. The ridge-type grating was chosen as a simple proof-of-principle model due to the straightforward relationship between ridge height and diffraction intensity. Understanding the reversible behavior of this photonic structure can then be extended to other grating geometries, for example, tooth-shaped,<sup>20</sup> sawtooth shaped,<sup>21</sup> and triangle shaped.<sup>22</sup> We have programmed a sub- $\mu\text{m}$  ratio optical grating that exhibits reversible magnitude changes of its diffraction intensity (up to about 36% modulation) when subjected to alternating changes in temperature. We have verified that this result is attributable to reversible modulation in the grating's ridge height and that it is repeatable over multiple cycles. By melting all crystalline regions within the sample, the grating structure can be erased, recovering the primary flat surface, which can then be reprogrammed to a new shape.

## EXPERIMENTAL SECTION

**Material Fabrication.** For this experiment we sought to fabricate the reversible optical element in a representative semicrystalline polymer poly(octylene adipate) (POA) as reported previously.<sup>14</sup> The chemical structure of end-functionalized POA is shown in Figure 1a. To utilize the best RSM behavior of POA, we synthesized POA with a number-average degree of polymerization (DP) of  $n = 13$  ( $M_n = 3500$  g/mol), which is known to exhibit significant shape reversibility.<sup>14</sup> In the previous work, we used the condensation polymerization between adipic acid and octylene diol to produce POA,<sup>14</sup> while in the present study, we have improved this synthesis by adipoyl chloride reacting with octylene diol. The new route provided a faster reaction and more accurate control of molecular weight distribution. This resulted in a higher  $T_m$  of 58 °C, compared to that of the previous synthesis, which was around 50 °C. Under the experimental ramping condition, a strain reversibility of 41% was observed when the shape-memory polymer was subjected to 15% uniaxial strain deformation (Figure S1, Supporting Information). Figure 1b displays a two-step thermosetting procedure that has been used to make an optical grating with reversible control over grating height. First, POA was mixed with 10 wt %  $\text{CHCl}_3$  and 1 wt % 2,2-diethoxyacetophenone. The mixture was

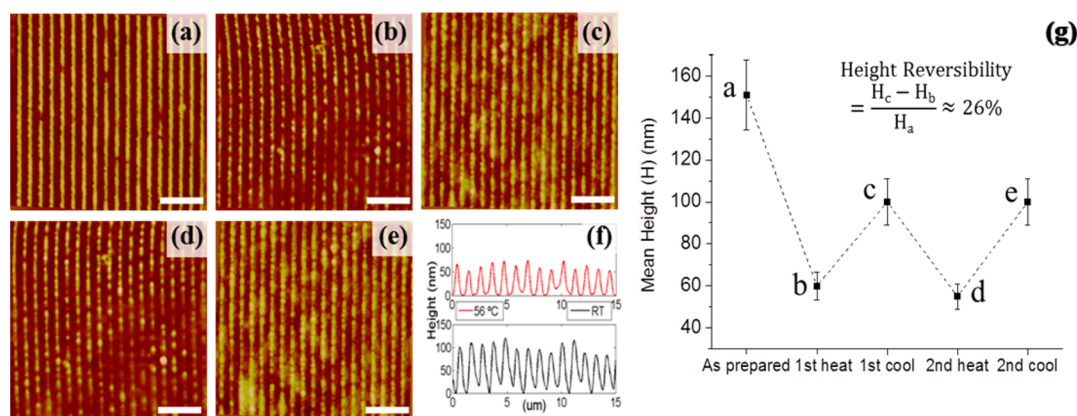
then injected into a Teflon mold, covered with a glass slide, and cross-linked with 365 nm UV light for 5 min. This produced a RSM substrate with an optically flat surface as the primary shape. The substrate was then annealed free-standing at 70 °C overnight to extract the remaining solvent and thermal history. Next, the substrate was heated to 70 °C, and the optically flat surface was pressed against a perfluoropolyether (PFPE) grating (pitch, 750 nm; ridge height, 250 nm; ridge width, 250 nm) followed by quenching in an ice bath. On separation of the substrate and the PFPE mold, the surface was in its secondary grating shape, which accurately replicated the PFPE grating.

**Optical Measurements.** Experimental measurements of the grating diffraction intensity were taken under illumination using light from a 633 nm He–Ne laser, which was incident at a 5° angle with respect to the sample normal; the experimental set up is shown in Figure S2 (Supporting Information). The 750 nm grating pitch was chosen, such that only the  $M = +1$  diffraction order will be measured, with sufficient angular space between the specular reflection ( $M = 0$ ). Planar diffused silicon photodiodes (United Detector Technology) with a spectral sensitivity from 400 to 1100 nm and a responsivity of  $\sim 0.4$  A/W at 633 nm were used to monitor the intensity of the first-order diffraction mode and the intensity of the incident beam in order to correct for power fluctuations. Incident beam intensity was monitored by splitting the initial beam with a 50/50 beam splitter. Simultaneously, the first-order diffracted light was monitored, and relative intensity was calculated by normalizing the diffracted beam intensity with the incident beam intensity. The temperature of the sample was controlled using a thermoelectric stage and a thermocouple directly in contact with the sample surface. To achieve RSM performance, instead of complete melting, we brought the POA gratings to a partial melting temperature ( $T_p$ ; Figure 1c) at a heating rate of 1 K/s, and then held for at least a minute before natural cooling at a slower rate dictated by the thermal equilibration at room temperature (RT).

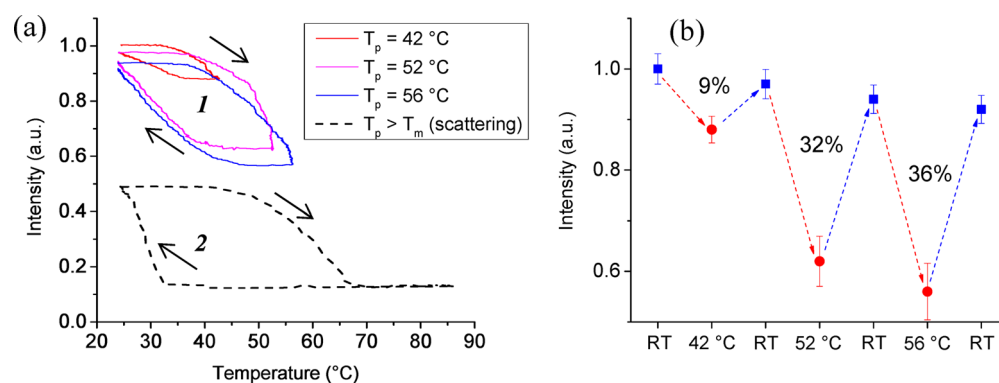
## RESULTS AND DISCUSSION

### Microscopic and Morphological Characterization.

Temperature-triggered variations of the grating topography were monitored in situ using an atomic force microscope equipped with a heating–cooling stage. In previous work, the maximum reversibility of POA was achieved when the partial melting temperature  $T_p$  was close to the melting peak  $T_m$ .<sup>14</sup> In the present work, we have therefore recorded AFM measurements for the same maximum reversibility cycle ranging from RT to  $T_p = 56$  °C. The ridge height was found to vary with temperature, while all other grating parameters remained constant. Figure 2a–c shows the first heating–cooling cycle from an as-prepared grating structure, Figure 2d,e shows the



**Figure 2.** AFM images (a) as prepared and at room temperature, (b) after heating to 56 °C at 1 K/s, and (c) after cooling back to room temperature. (d) Second heating to 56 °C at 1 K/s and (e) after subsequent cooling back to room temperature. All scale bars are 5 μm. (f) Height averaged line profile of the sample during one heating cycle (top) at 56 °C and (bottom) cooled to RT. (g) The corresponding AFM mean ridge height was averaged over 180 line profiles per AFM image. The height reversibility is calculated using the mean heights of corresponding AFM images.

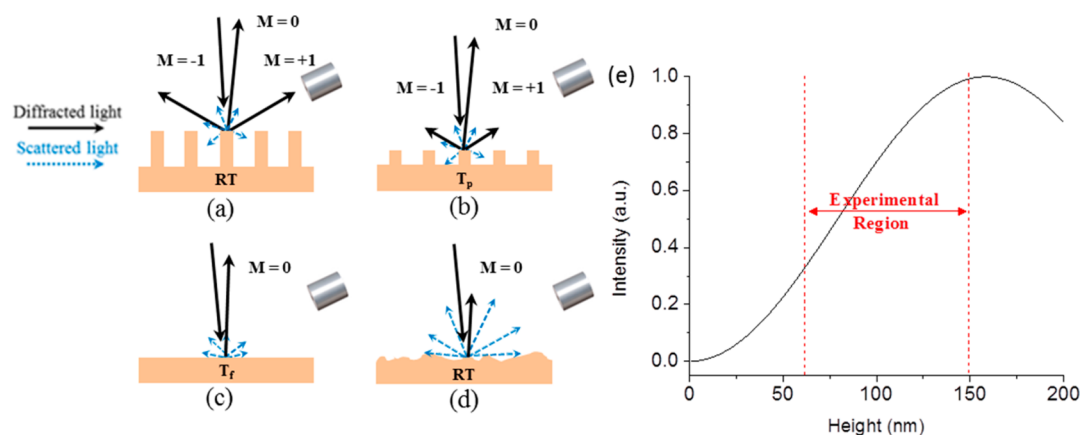


**Figure 3.** (a) Optical intensity of a diffraction spot as temperature was varied (arrows showing ramping direction). Region 1: Optical intensity can be reversibly controlled within different cycles with  $T_p$  kept below  $T_m$ . Region 2: When  $T_p$  is increased above  $T_m$ , the grating is greatly erased and nonrecoverable. The intensity drops significantly as the temperature increases to  $T_f$  ( $T_f = 70$  °C). Now the surface returns to its flat primary shape and the intensity changes upon cycling are due to melting/crystallization-induced scattering. (b) Optical reversibility was calculated for three  $T_p$  cycles. A maximum optical reversibility of 36% was achieved when  $T_p$  was set at 56 °C, which is close to  $T_m$ .

second heating–cooling cycle, indicating good repeatability. Average line profiles of the sample at 56 °C and after cooling to RT are shown in Figure 2f. Average ridge height analysis (Figure S3, Supporting Information) of the line profiles shows the height reversibility is around 26% (Figure 2g). This microscopic reversibility of the grating feature is less than the bulk reversibility (~41%) of a polymer film when subjected to 15% uniaxial strain deformation. The discrepancy between bulk and microscopic reversibility may be due to plastic deformation and crystallization. We ascribe the observed plastic deformation to the nonuniform strain distribution generated by the embossing process used for shape programming, which possibly induced the nonerasable grating artifacts present in a few locations even after complete sample melting (Figure S4, Supporting Information). In addition, we know from previous work that freshly molten chains tend to recrystallize into large spherulites (~10 μm),<sup>14</sup> which interfere with crystallization in the nanoscale confinement of the grating and lead to a rough surface structure.

**Reversible Optical Properties.** Variations in the optical properties of the RSM grating due to the observed change in surface topography were explored. Figure 3a depicts a reversible change in diffraction intensity upon the corresponding variation in substrate temperature (Figure 1a, Region 1). Before reaching

40 °C, the change in intensity is minimal. This finding agrees with the previous results indicating that the onset of shape recovery occurs only after melting of at least ~10 wt % of the initial crystallinity.<sup>14</sup> Above 40 °C, the diffraction intensity begins to decrease due to the onset of shapeshifting (Figure 4b). Upon continued heating to a partial melting temperature  $T_p = 42$  °C, the diffraction intensity continues to decrease. Upon cooling, the intensity recovers toward its initial value at RT (Figure 4a), indicating good optical reversibility (Figure 3b). When a POA grating is heated to a higher temperature ( $T_p = 52$  or 56 °C), the observed intensity modulation increases as well (Figure 3b). For each  $T_p$ , we heated and cooled a single POA grating sample multiple times between RT and  $T_p$ , and observed that the intensity change was repeatable over multiple cycles. Typical experiments included 2–3 cycles per temperature, with less than 5% variation in optical intensity. Further cycling at a single  $T_p$  resulted in a loss of ~10% of optical intensity over 25 cycles. In Figure 3a, only one cycle for each  $T_p$  is shown for clarity. By varying  $T_p$ , we located the optimal melting temperature to maximize reversibility: The maximum optical reversibility is ~36% and is found when partial melting  $T_p = 56$  °C, which is near the  $T_m$  (Figure 1c), and is consistent with the previous RSM study.<sup>14</sup> As we explain later, when a



**Figure 4.** Diffraction and scattering intensity change with temperature. The first diffraction order was monitored as the grating was (a) cooled to RT and (b) heated to a partial melting temperature  $T_p$ . Arrow length indicates relative intensity, which relates to grating height. (c) At  $T_p$ , the surface returns to optically flat, the detector only picks up scattering signal, and (d) when cooled back to RT, crystals form in an unrestricted fashion, resulting in an optically rough surface that more readily scatters light. (e) Theoretical calculations indicate a sine-squared relationship between grating height and grating efficiency between 10 and 200 nm. As grating height decreases from  $\sim 150$  to 60 nm, the measured intensity should decrease in near linear fashion.

sample is heated to  $T_p > T_m$ , the grating is largely erased and the shapeshifting process is nonreversible.

The optical reversibility (OR; Figure 3b) is calculated as:

$$\text{OR} = \frac{I_{\text{RT,end}} - I_{T_p,\text{partial melt}}}{I_{\text{RT,start}}} \quad (1)$$

where  $I_{\text{RT,start}}$  is the intensity of diffracted light (first diffraction order) by the grating at room temperature before heating;  $I_{T_p,\text{partial melt}}$  is the intensity of the diffracted light at a temperature of partial melting ( $T_p$ );  $I_{\text{RT,end}}$  is the intensity after cooling back to room temperature. The first diffraction order was measured at  $68^\circ$  from the grating normal, and it was more than 10 times brighter than light detected in other directions due to some minor random scattering. Therefore, the observed optical reversibility is mainly attributable to changes in height of the grating ridges as a result of the RSM behavior. As the temperature increases, a sufficient fraction of crystalline scaffold has melted, which causes the grating to return toward its flat primary shape. Within the range  $T_p < T_m$ , enough crystallites remain to recover the embossed secondary shape upon cooling through self-seeded recrystallization, and the diffraction efficiency shows excellent reversibility and good repeatability over multiple cycles. Therefore, by referring to  $T_m$  as an upper temperature and lower grating height limit, a proper programming protocol can be determined for a desired reversible photonic actuation. The intensity never returns completely to the as-prepared programmed shape due to partial relaxation of the chemical network during recrystallization after each heating-cooling cycle. Note that the strained chemical network always tends to return to its equilibrium unperturbed state (primary shape).<sup>9,14</sup> However, the natural trend of thermodynamic equilibration is reversed by the kinetics of recrystallization of the constrained network strands, which is biased by the remaining crystallites carrying the memory of the programmed secondary shape.

When  $T_p > T_m$ , the POA grating enters a new behavior regime 2 (Figure 3a). In this regime, a majority of the crystallites have melted, allowing the chemical network to relax to its thermodynamically preferred shape dictated by the chemical cross-links and causing the sample to return toward its

flat, primary shape. Upon heating to  $85^\circ\text{C}$ , the grating is largely destroyed and nonrecoverable with only some small residues of grating structure (less than  $10 \times 10 \mu\text{m}$  over a  $50 \times 50 \mu\text{m}$  scan window; Figure S4, Supporting Information) and the surface returns to its original flat morphology. The optical intensity drops to a minimum value dictated by intrinsic scattering in the substrate.

**Separation of Diffraction and Scattering.** In Figure 3a Region 2, the optical response appears to be comparable in magnitude to that of Region 1, but the distribution of the detected light is different for both regions. In Region 2, the sample has been heated beyond  $T_m$ , and the periodic grating is completely destroyed, so the majority of the light is simply reflected by a flat melted surface in a specular fashion, missing the detector still located where the first diffraction order used to propagate (Figure 4c). When the sample is cooled from its fully melted state, the intensity increases when  $T_c = 37^\circ\text{C}$  is reached, and the sample undergoes a random crystallization without trace of any shape memory effect. This random crystallization gives rise to pronounced light scattering in all directions, including that of the detector (Figure 4d). As the surface becomes optically rough, the light that was previously diffracted and specularly reflected now contributes to the scattered light. Intensity contributions from residual grating due to plastic deformation are minor, as the areas are randomly distributed over the entire sample and constitute a small percentage of surface ( $<10\%$ ). It should be noted that this behavior is in distinct contrast with the modulation in Region 1, where the grating exists at all times and the bulk of the detected light is the first diffraction order with a minimal contribution from scattered light ( $<10\%$ ) (Figure S5, Supporting Information). We have conducted a separate study to distinguish individual contributions from diffraction and scattering while a grating is present (Figure S5, Supporting Information). The random scattering contribution in Region 2 is due to polymer crystallization yielding a heterogeneous assembly of randomly oriented crystallites with a size distribution ranging from 10 to 1000 nm. This resulted in isotropic scattering, with minor variances of 1–2% observed. This result may offer an alternative way to study crystallization-induced surface roughness.

**Theoretical Diffractive Mode Intensity.** The magnitude of the diffraction intensity change can be understood by analyzing the effect of the grating height. When a monochromatic laser beam is incident on a reflective diffraction grating surface, the reflected light interferes in a phase-sensitive manner that depends on the grating spacing, height, and overall geometry and produces a series of bright diffraction modes. For an ideal diffraction grating, the intensity of zeroth- and first-order diffraction modes can be represented by eqs 2 and 3, respectively.<sup>23</sup>

$$I_0 \propto \cos^2(2\pi\delta/\lambda) \quad (2)$$

$$I_1 \propto \sin^2(2\pi\delta/\lambda) \quad (3)$$

where  $\delta$  is the height of the grating, and  $\lambda$  is the wavelength of the laser beam. Figure 4e shows that the diffraction efficiency of the first order diffraction mode increases with the grating height monotonically when the height is below 160 nm, which offers a wide operation range for a possible application. When the RSM grating is heated, its ridges decrease in height, reflecting weaker first-order diffraction mode and higher zeroth-order diffraction mode. The slightly nonlinear optical response of the simulated grating efficiency, may contribute to the discrepancy between the height and optical reversibility (cf. Figures 2g and 3b).

## CONCLUSION

Reversible shape memory (RSM) has been utilized to precisely replicate and control the shape of sub- $\mu\text{m}$  features used in optical applications. This was determined by monitoring the diffraction efficiency as the patterned RSM substrate was subjected to heating-cooling cycles, within the range  $T_p < T_m$ . The maximum optical reversibility was determined to be 36% when  $T_p$  is near  $T_m = 56\text{ }^\circ\text{C}$ . The diffraction intensity can be controlled and always returns within 10% of the original intensity, unless  $T_p > T_m$ . The approach presented for the fabrication of the gratings can be applied to more complicated optical nanostructures for use in optical analytical equipment such as active blazed gratings. Furthermore, monitoring optical scattering intensity was also found to be a viable way to observe melting and crystallization-induced roughness on the surface of semicrystalline polymers. Additional studies need to be performed to determine relationships between crystallite size and scattering effects.

## ASSOCIATED CONTENT

### Supporting Information

DMA tensile test of bulk poly(octylene adipate), grating height analysis methods, surface morphologies after complete melt, and scattering data of SMP gratings. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b02688.

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## Notes

The authors declare no competing financial interest.

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## Supporting Information

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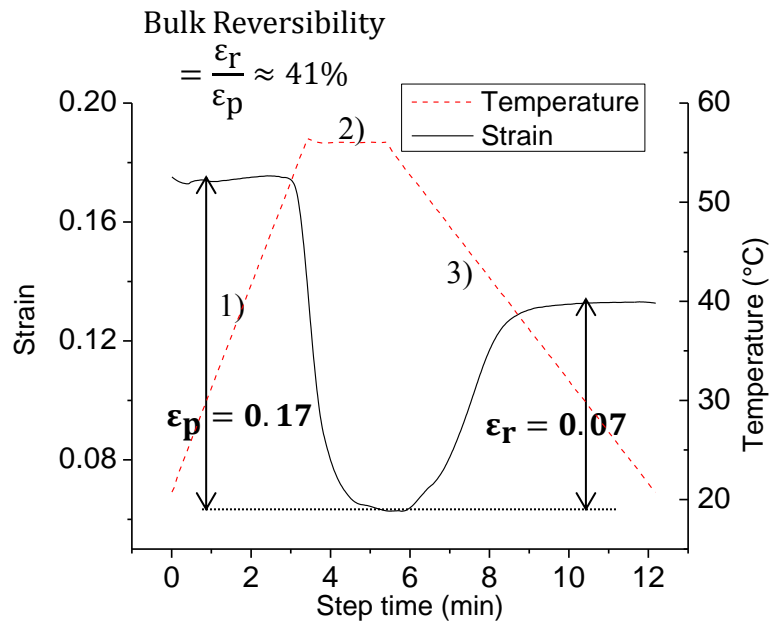
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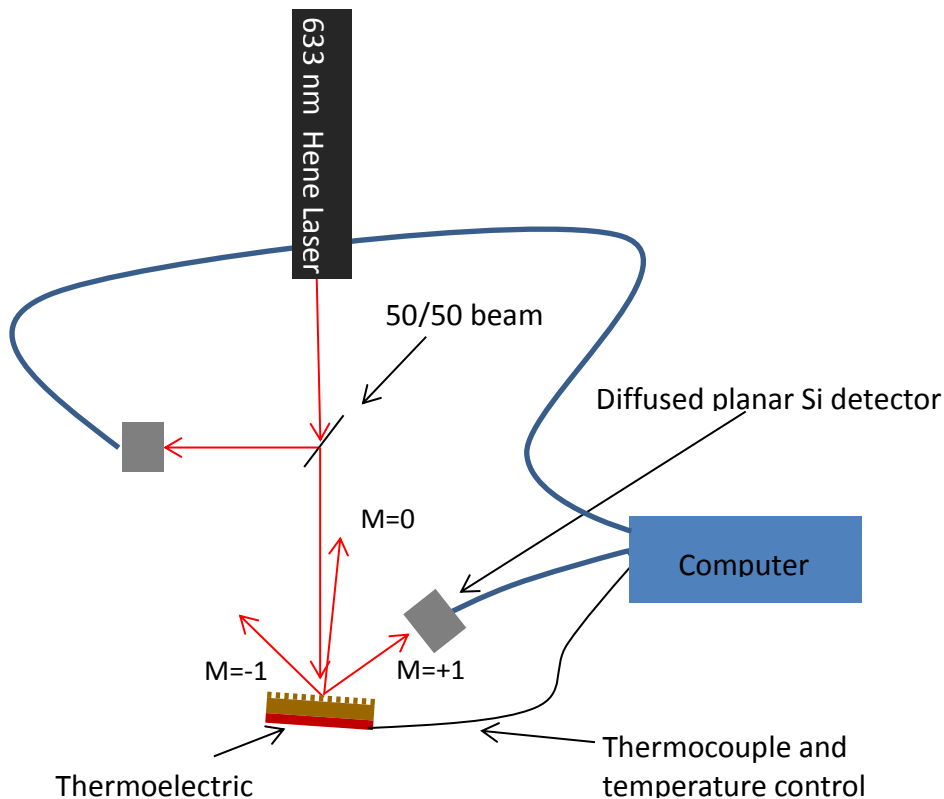
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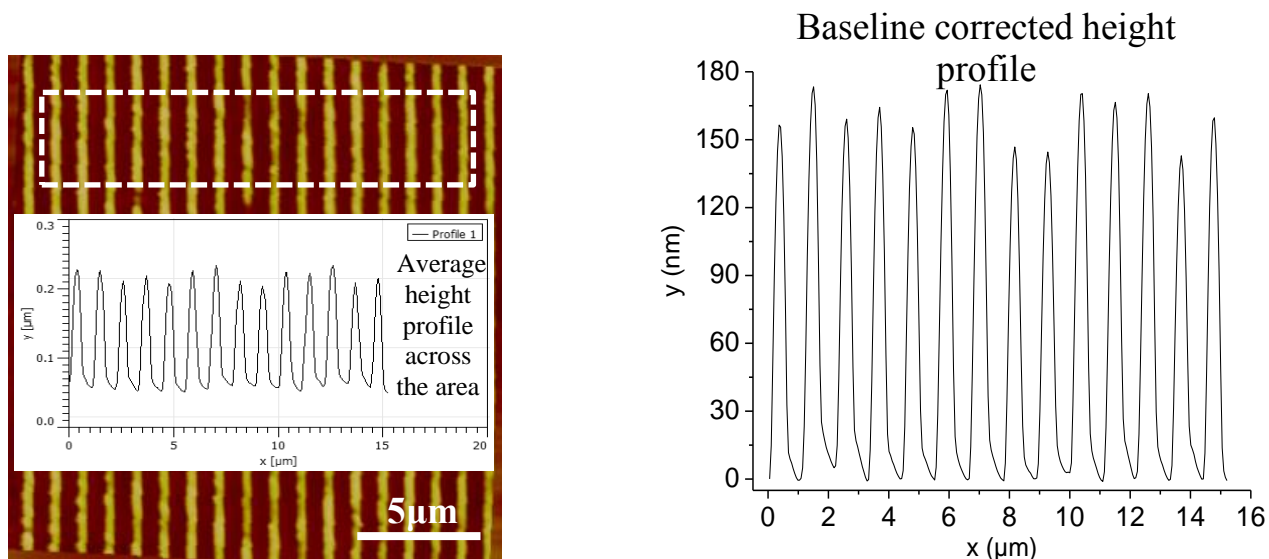


**Figure S1.** A dogbone bulk sample’s maximum reversibility was characterized by DMA tensile test as 41%, where  $\epsilon_p$  was defined as programmed strain and  $\epsilon_r$  as recovered strain. Partial melting temperature  $T_p$  was near  $T_m = 56$  °C. The temperature ramp has similar rate as the optical experimental set up: 1) Heat from 20 °C to 56 °C (10 °C/min); 2) Wait 2 min at 56 °C; 3) Cool from 54 °C to 20 °C (5 °C/min).



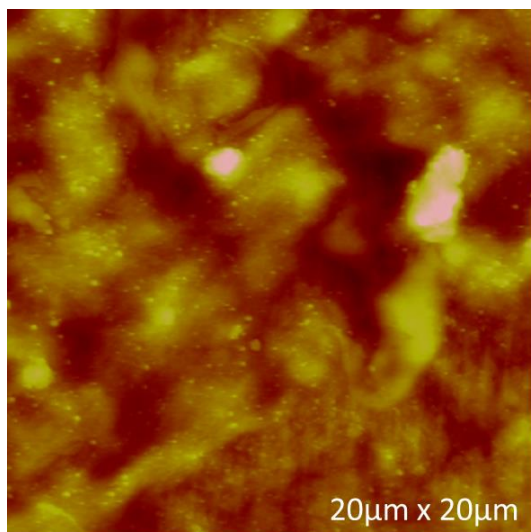


**Figure S2.** Optical measurement set up, for measuring the diffraction intensity. The incident beam is first, passed through a 50/50 beam splitter, in order to monitor the incident power. The beam then impinges on the surface of the SMP grating. The resultant first order diffraction intensity is monitored via a diffused planar Si detector. The SMP grating is placed in contact with the thermoelectric stage and the temperature of the sample was controlled via Labview and monitored with a thermocouple.

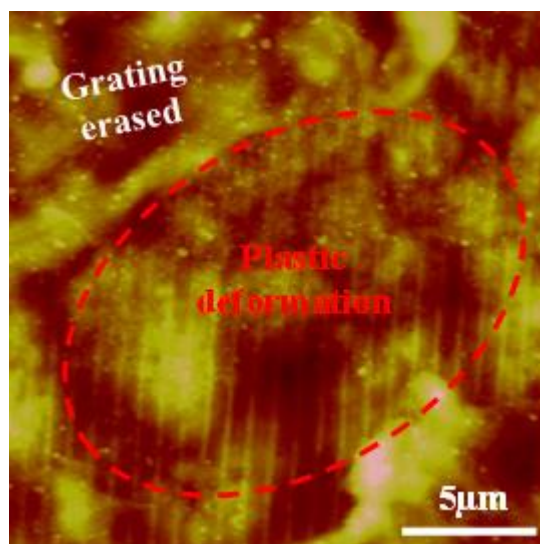


**Figure S3.** AFM height analysis of grating topology. A cross-sectional area was chosen to be averaged and from this area 180 line profiles are averaged to compile the averaged line profile. The averaged line profile is then baseline corrected and the average ridge height is calculate

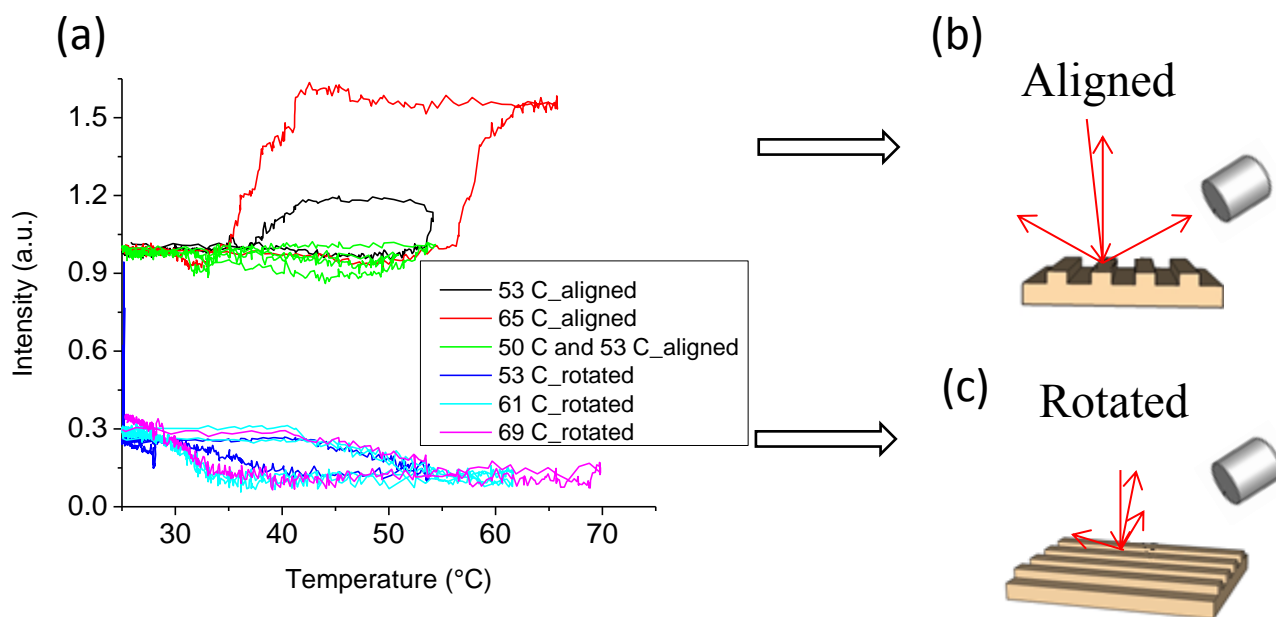
(a)



(b)



**Figure S4.** An SMP piece was heated to 80°C, a complete melting temperature, then cooled back to RT. Most gratings structures were erased and surface returned to the original shape (a), however a few spots turned out to remain grating structure due to plastic deformation (b). The crystallization induced random roughness on the erased area was also observed.



**Figure S5.** Optical measurements (a) of a permanent grating, with no programmed secondary memory. When the 1<sup>st</sup> diffraction order is (b) aligned with the detector and the temperature is varied, the permanent grating undergoes an internal realignment as the crystals melt which smooths the grating surface. This results in a more efficient grating, increasing the observed intensity. The permanent grating is then rotated 90° (c) and the detector only picks up scattered light as the grating is cycled. In this measurement the modulation in intensity is due to the crystallites melting and recrystallization during cycling.

In this study a permanent grating with no secondary memory is cycled to determine the contribution of scattered light while a grating remains. A SMP prepolymer mixture was poured into a Teflon flat mold with a PFPE replica of the silicon grating placed on the bottom of the mold. After UV curing, the bottom side of the sample has permanent grating structure. Measurements of a permanent shape grating, with no programmed secondary memory, were performed in order to determine the difference in the intensity of scattered light versus diffracted light while a grating is present. The SMP permanent grating was first aligned with the silicon detector and cycled through various temperatures below and above  $T_m$ . Below  $T_m$  there is almost no change in the intensity of the diffraction spot however at  $T_m$  and above  $T_m$  there is an increase in intensity

which can be attributed to a majority of crystallites melting and the grating returning to its as molded, perfectly ordered, shape. When the sample is rotated 90 degrees and the detector only detects scattered light, the intensity drops and a modulations of ~10% is seen for scattered light at  $T_m$ . It can be observed that while a grating is present on the sample surface, any intensity modulation observed is due mainly to shape shifting of the grating and not scattering from crystal melting and recrystallization.

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