Grayscale digital light processing 3D printing for highly functionally graded materials

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Three-dimensional (3D) printing or additive manufacturing, as a revolutionary technology for future advanced manufacturing, usually prints parts with poor control of complex gradients for functional applications. We present a single-vat grayscale digital light processing (g-DLP) 3D printing method using grayscale light patterns and a two-stage curing ink to obtain functionally graded materials with the mechanical gradient up to three orders of magnitude and high resolution. To demonstrate the g-DLP, we show the direct fabrication of complex 2D/3D lattices with controlled buckling and deformation sequence, negative Poisson’s ratio metamaterial, presurgical models with stiffness variations, composites for 4D printing, and anti-counterfeiting 3D printing.

INTRODUCTION

Three-dimensional (3D) printing or additive manufacturing (AM) attracts tremendous attention and has become a promising manufacturing technology that will revolutionize our perception of how a part is designed and fabricated. Its application has expanded from rapid prototyping to tissue engineering (1, 2), electronic devices (3, 4), soft robotics (5, 6), and high-performance metamaterials (7–9). However, most 3D printing methods can only print parts with one single material property or multiple discrete properties without control of complex mechanical gradients. Most structures in nature, such as fish scale (10) and tendon-to-bone (11), are made of materials with markedly different properties. The so-called functionally graded materials (FGMs) (12) have drawn substantial research interest because of their advantages in improving the mechanical robustness and flaw tolerance (13). Because of this, 3D printing of FGMs with widely tunable properties in a single printing process becomes increasingly important and has been actively studied recently.

The most successful example is the Polylet method, which uses multiple inkjet printheads to simultaneously deposit different materials on the printing bed (14). However, the Polylet method has some notable drawbacks, including high equipment cost, stringent resin property requirement, limited material choices, and relatively low resolution (>200 μm in multimaterial printing mode) (15). For these reasons, many other 3D printing methods were actively pursued. For example, extrusion-based 3D printing technologies, such as fused filament fabrication (16) and direct ink writing (17, 18), were used to create multimaterial parts via multiple nozzles. However, these methods typically suffer from slow printing speed. In addition, in the approach using multiple nozzles, it is difficult to obtain properties that vary continuously from one to another. Digital light processing (DLP) 3D printing method based on digital micromirror devices (DMDs) emerged in recent years as a new rapid and high-resolution AM approach. It cures a polymer resin layer at one time and is therefore very fast. This advantage becomes more significant when the cross-sectional area of a part increases. More recently, the emergence of CLIP (continuous liquid interface production) is a true breakthrough as it offers the fastest 3D printing technology that is close to the production level (19). However, DLP is generally regarded as unsuitable for printing parts with multiple properties as it uses a single vat of resin. Methods were developed in the past to use multiple vats and switch between different vats (20) or to use grayscale light (21, 22) for multimaterial printing. However, these methods have the notable drawbacks of either slow speed, or a narrow range for tunable properties, or residual monomers for practical uses.

Here, we report a novel 3D printing ink and a grayscale printing method for graded materials with widely tunable mechanical property gradients using the single-vat grayscale DLP (g-DLP). The hybrid ink was first cured by grayscale light patterns to form a structure with location-specific properties followed by a second-stage thermal curing to simultaneously eliminate most of the residual monomers and enhance the property gradients. Using this method, broadly tailored functional gradients, such as modulus up to three orders of magnitude and glass transition temperature up to 60°C, within a layer and a part can be achieved. We demonstrate several novel applications of g-DLP–printed FGMs, such as 2D and 3D lattice, cellular structures, and metamaterials for functional applications.

RESULTS

Digital materials by g-DLP

We developed a novel two-stage curing hybrid ink system to achieve the single-vat g-DLP 3D printing. As a demonstration, a hybrid ink containing bisphenol A ethoxylate diacrylate (BPADA), glycidyl methacrylate (GMA), n-butyl acrylate (BA), a diamine cross-linker [poly(propylene glycol) bis(2-aminopropyl ether); D230], photoinitiators (Irgacure 819) together with photo-absorbers (Sudan I) was made. In the single-vat g-DLP 3D printing, as shown in Fig. 1A, images with grayscale patterns, which under monochromatic setting correspond to light intensity, were used to cure the resin in a layer-by-layer manner. Akin to CLIP, an oxygen-permeable window was exploited to enable easy separation of the cured part from the window; this can potentially enable fast printing speed. The designed structure was first sliced into images that correspond to individual printing layers. Each image was then processed with a MATLAB code to generate the grayscale distribution according to the desired properties. The images of individual layers with grayscale patterns were then passed to the ultraviolet (UV)
projector for printing. The acrylates first undergo radically induced photopolymerization, which leads to the formation of a polymer network that holds the shape of the printed part. The cross-linking density and the modulus of the materials decrease with the increasing grayscale percentage. It is noted that the underexposed “green” parts by conventional grayscale curing suffer from weak mechanical properties and toxic unreacted monomers (21–25). We use the two-stage curing mechanism to simultaneously eliminate most of the residual monomers and boost the mechanical gradients of the green parts. The GMA monomer and diamine cross-linker play a critical role in the thermal curing process. The results of the model reaction between GMA and D230 suggested that the diamine cross-linker would react with double bonds (acrylate) and epoxide by Michael addition reaction and ring opening reaction, respectively (figs. S1 to S3). The detailed reaction behavior in the grayscale cured materials will be discussed later.

The effect of grayscale on the photopolymerization of the hybrid ink was investigated. The image grayscale derived from the RGB (red-green-blue) value was normalized to obtain grayscale percentage (denoted as $G$ value) from 0% (full intensity) to 100% (full dark) (fig. S4A). The dependence of light intensity on grayscale was measured, showing a nonlinear dependence. We used the degree of conversion to indicate the reaction content of the double bonds in acrylates. The curing depth or the position of the curing front was calculated by the following equation (26, 27)

$$
\tilde{z} = \frac{\ln \left( \frac{K_{tot}}{\ln(1-p_c)} \right)}{\mu_0}
$$

where $K$ is the reaction constant, $I_0$ is the light intensity, $t$ is the curing time, $p_c$ is the critical conversion, and $\mu_0$ is the light attenuation coefficient of the resin. The curing thicknesses of the samples with different light irradiation times were measured via the G50 light on the hybrid ink sandwiched between two glass slides. The $p_c$ value of 15%

**Fig. 1.** g-DLP 3D printing of FGM via two-stage curing. (A) Schematics showing the g-DLP printing of graded material via a two-stage curing process. A hybrid ink was used for DLP 3D printing first followed by thermal curing the printed part in a heating oven. (B) Predicted normalized conversion of cured material under different grayscale light with only one exposure (solid lines) and multieposure (dashed lines) by the model using the exposure time of 20 s and curing thickness of 60 μm per layer. (C) Gel fraction of hybrid ink after the first- and second-stage curing. (D) Tensile stress-strain curves of printed materials using different grayscale during printing (sample size, >3). (E) Young’s modulus and glass transition temperature of printed materials as functions of grayscale. (F and G) Design, print part under bending, and corresponding FEM simulation of graded materials enabled by g-DLP using a discrete gradient (F) and a continuous gradient (G) grayscale pattern. Scale bars, 5 mm.
was estimated from Fourier transform infrared spectroscopy (FTIR) data showing that a gel can be formed at the conversion over 15%. The $K$ and $\mu_0$ values were determined to be 0.01 cm$^2$ mW$^{-1}$ s$^{-1}$ and 8.05 mm$^{-3}$, respectively (fig. S4B).

Using the above reaction kinetics model, the depth-dependent reaction conversion was calculated on the basis of the normalized conversion result using light dose ($D$) (fig. S4C). Figure 1B (solid lines) shows the conversion using different grayscale light for photocuring ($t = 20$ s) within one layer (60 μm) by the model prediction. The normalized reaction conversion gradually decreases with increasing thickness and increasing grayscale percentage. However, during the g-DLP printing process, each layer experienced multiple light exposures due to light penetration in the layer-by-layer printing process. The actual conversion in a layer is thus higher than that from the single layer printing and should be calibrated based on the effective $D$. The detailed evaluation of $D$ can be found in the Supplementary Materials. The effective conversion under different grayscale by multieposure was calculated by (24)

$$p_n(z) = 1 - \exp[-KD(z, n)], \quad D(z, n) = \sum_{m=1}^{n} I_m(z) \Delta t$$

where $p_n$ is the conversion of the material during $n$th light radiation, $I_m(z)$ is the light intensity at the position after curing $m$ layers, and $\Delta t$ is the light exposure time of each layer. Figure 1B also shows the normalized conversion of material in one-layer thickness under multieposure under different grayscales (dashed lines). It is found that despite the effect of multiple exposures on the reaction conversion, the general relation between the grayscale and conversion remains similar; however, a higher grayscale (G value) should be used in 3D printing to achieve similar material properties by the single layer exposure (fig. S4D). Note that the printing resolution of g-DLP in the $x$-$y$ plane is determined by both the pixel size (50 μm here) and the printing parameters, such as layer curing time and light intensity. In particular, the pixel grayscale value has a great influence on the resolution. For example, an array of pixelated grayscale light from G0 to G85 enabled the printing resolution from 50 to 120 μm (fig. S5). A lower grayscale value of the pixel leads to partial overcuring as indicated by the larger physical dimension than the pixelated light pattern size. It is noted that the property transition is continuous for both continuous and discrete grayscale pattern designs. Figure S5 also shows that there is a transition region between the different grayscale cured parts (G0 and G73). However, this transition is very narrow and steep for the discrete grayscale design (50 to 100 μm). The interface between the graded parts is strong as it is enabled by the chemical bonding in the transition region. These results suggest that a high printing resolution in the $x$-$y$ plane can be obtained. In our g-DLP system, although light leakage may cause some reduction of the resolution, this can be compensated by software or using an optical system with smaller optical magnification. Moreover, because of the compatibility of the hardware systems with the DMD projector, this approach can be extended to projection microstereolithography with a resolution of a few micrometers in the $x$-$y$ plane (8). The physical resolution in the $z$ axis can be tuned by changing the slicing/printing thickness and even achieve a high-resolution matching CLIP system (19). Light penetration for the resin in the $z$ axis can be suppressed by increasing the photo-absorber content so as to improve the $z$ resolution of printed material properties.

As mentioned above, the first-stage photocuring by grayscale light would result in graded parts with variation in reaction conversion or residual monomers. The reaction conversion can also be evaluated by gel fraction indicating the percentage of cross-linked species in the material. Figure 1C shows that, after the first-stage photocuring (or 3D printing), the gel fractions are 86 and 65% for G0 and G70, respectively. However, unreacted monomers would further be polymerized during the thermal curing stage to enhance the network integrity. After the second-stage curing, the gel fractions increase to 93 and 88% for G0 and G70, respectively. More specifically, the photopolymerized GMA in the polymer network with dangling epoxide side groups would react with the amine cross-linker to effectively enhance the cross-linking density for parts with intense photocuring; the unreacted free GMA and other acrylates would react with diamine cross-linkers contributing to enhancing chain branches, which predominantly occur in the parts with less light exposure. The chemical structure evolution during the two-stage curing (printing and thermal curing) was verified by FTIR (fig. S6). During the photocuring stage, the acrylates in the hybrid ink were photopolymerized with some residual monomers trapped in the network as indicated by the reduction and existence of the signal from double bond vibration. After the second-stage thermal curing, the signals from both epoxide and acrylate decrease obviously, suggesting the occurrence of the reaction between the diamine cross-linker and residual monomers. It should be noted that, as the thermal curing temperature is less than 120°C, the self-initiation of acrylate polymerization is relatively weak (28). Most of the previous photothermal two-stage curing systems generate a uniform (semi-)interpenetrating polymer network or phase-separation structure (29, 30). By contrast, using the novel two-stage curing resin here, a hybrid network with tunable network cross-linking density and chain architecture was obtained. The obtained graded materials without toxic residual monomers make it possible for practical uses.

The differences in the network architecture and cross-linking density of the materials lead to widely tunable mechanical and thermomechanical properties. We first evaluated the mechanical properties of the printed materials. The samples were printed using a single grayscale light for the first-stage curing. With only the first-stage photocuring, the Young’s modulus spans only a few times from 1.5 to 8.1 MPa when the grayscale varies from G80 to G0 (table S1), which is not enough for broader applications. The second-stage curing markedly increases the property span. Figure 1D shows the tensile stress-strain behaviors of printed samples after the two-stage curing. Overall, all the samples can be stretched by more than 25%. For the samples with brighter light (low grayscale value), yielding behaviors can be observed at ~5% strain. Figure 1E shows Young’s modulus and glass transition temperature ($T_g$) as functions of grayscale percentage. The properties vary from a soft rubber with Young’s modulus as low as 1.4 MPa (G93) to a glassy polymer with Young’s modulus as high as 1.2 GPa (G0), a contrast of nearly three orders of magnitude. The thermomechanical properties are also widely tunable, and $T_g$ can range from 14° to 68°C as indicated by the tan δ peak temperature (fig. S7). Figure 1E also shows the continuous dependence of modulus and $T_g$ as functions of grayscale percentage, offering the possibility to create digital materials by controlling the grayscale (which can also be digitized). The property distinction was mainly derived from different network architectures. The cross-linking density decreases continuously with increasing grayscale level for both curing stages (fig. S7). Note that the acrylate double bond can form two chemical linkages on the two ends by radically induced photopolymerization; however, it can produce only one bond linkage by Michael addition and ring opening reaction. The cross-linking density distinction in the grayscale light-cured parts is mainly determined by the photocuring stage, which is further enhanced by thermal curing.

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For example, after the thermal curing stage, the cross-linking densities increase from $1.04 \times 10^3$ to $2.23 \times 10^3$ mol/m$^3$ and from $0.19 \times 10^3$ to $0.78 \times 10^3$ mol/m$^3$ for G0 and G80, respectively. $T_g$ and Young’s modulus are more influenced by the thermal curing stage. Comparing with the most conventional heterogeneous graded materials associated with the variations in local chemical compositions/constituents, this is a novel homogeneous graded material with variations in network architectures. Homogeneous FGMs with location-specific network cross-linking density, chain architecture, and $T_g$ can be directly fabricated for multifunctional applications.

To demonstrate the capability of g-DLP printing, we printed samples of simple geometry with graded properties. In Fig. 1F, a discrete gradient grayscale pattern with the middle part of G80 and the two ends of G20 is used to print a stripe, whose middle section is much softer (~11 MPa) than the two ends (~880 MPa). The printed sample only bent in the middle upon applying a load from the top (movie S1). This deformation was predicted by finite element modeling (FEM) simulation with high accuracy. Similarly, a continuous gradient grayscale pattern enabled the fabrication of a continuously graded material (Fig. 1G), which bent with a continuously changing curvature upon the application of a point load. The experiment and simulation results of single-point bending behavior are comparable.

**Graded metamaterials for multifunctional applications**

One advantage of the DLP 3D printing method is the printing of hollow structures without or with little supporting structures to fill in the holes in the structures. We explored the design and fabrication of lattice or cellular structures via g-DLP. As shown in Fig. 2A, a 2D lattice architecture matrix (G20) with a grayscale pattern of a triangular region (G80) and blank region underneath was designed and printed. The deformation during compression mainly occurred in the triangular region with soft material where the space under the triangular band showed little deformation (movie S2), which provided a shield that protects the material (as shown by a puppy model) under this region. This controlled buckling can enhance the energy absorption capability as indicated by the stable stress drop in the stress-strain curve. The FEM simulation also predicted the experimental results well. It is also noted that most trusses in the G80 region broke after compression; the unbroken parts of the trusses showed some residual deformation. Figure 2B shows a 2D cellular solid comprising an elastomer matrix (G85) with bias distribution of rigid components (G50) surrounding an array of voids. The design of the 2D periodic porous structures using the graded materials enables marked pattern transformations and negative Poisson’s ratio under compression (movie S3). Unlike other examples of auxetic materials derived from the elastic instability above a critical value of an applied strain (31), our design enables Poisson’s ratio in the whole range of compression load as indicated by the linear stress-strain curve. The FEM simulation suggests that the dispersed hard rectangular regions (G50) near the voids embedded in the soft matrix (G80) can redistribute the strain and control the deformation under compression.

We also designed a 3D lattice structure, as shown in Fig. 2C, where each lattice layer was assigned with different grayscale of G70, G55, G40, and G0, respectively. The printed lattice structure shows a high resolution with a clean appearance. The compression tests were performed in different directions (movie S4). When compression was along the graded layer direction (x axis), the deformation was homogeneous across the thickness, and the lattice shows high initial stiffness but would fail quickly (Fig. 2D). However, when compressing perpendicular to the soft layer (z axis), this structure deformed sequentially. As shown in Fig. 2E, the softest layer (G70) was completely squeezed, followed by the squeezing of the second layer (G55) and then the third layer (G40). Because of the sequential deformation, the lattice showed relatively low initial stiffness but could be compressed by a significantly larger reversible strain (over 75%) (Fig. 2F). Such a multilayer structure showed that a sequential deformation behavior can be used for energy absorption.

The graded material properties from the g-DLP printing can be harnessed to print presurgical planning models (32). We demonstrated the potential of using the g-DLP technique to print tissue-like structures, which have not only the shape and the microstructure but also the similar feeling of stiffness. As shown in Fig. 2G, a limb-mimic structure with G0 as hard bone, G88 as soft muscle, G70 as skin, and hole (blank) as the blood vessel was designed. The printed limb-mimic structure showed a high resolution and a good finish. Because the majority of the part was made of soft “muscle,” the limb can be easily deformed by gently squeezing the material in the thickness direction (x axis). On the other hand, the “bone” region (around the hollow channel in the middle) retains its shape and was stable during the compression process (Fig. 2H). This limb-mimic structure can hold 1 kg of weight (nearly 230 times of its own weight) across the length direction (z axis) without obvious bending (Fig. 2I). This is because the hard material as a bone embedded in the soft matrix enables excellent stiffness of the structure. Similarly, a small-scale artificial limb structure with soft muscle (G85) and hard bone (G0) can be designed and printed by the g-DLP method (Fig. 2J). The widely tunable mechanical gradients enabled by the g-DLP 3D printing can satisfy not only customized architectures but also patient-specific physical properties. This advantage offers the great potential for the g-DLP method to be used for presurgical models (33).

**Sequential shape memory polymer components and 4D printing**

Because the g-DLP-printed material has a tunable $T_g$ ranging from 14° to 68°C, it can be used as shape memory polymers (SMPs) with different $T_g$s, which can exhibit shape memory effects with different actuation temperatures (34). Figure 3A shows the design of a helical pattern, whose panel portion is assigned with a grayscale of G20 and whose corners (or hinge) are assigned different gray scales ranging from G20 to G80. After printing and postprocessing, a helical component was obtained. We heated it to 60°C and opened it to a shape close to a straight line followed by cooling it down in ice water to fix the straight shape. This finished the programming step. Upon heating to ~60°C, the sample recovered to its spiral shape with the hinges folding sequentially (Fig. 3B and movie S5), which permitted the component to fold back to its original helical shape. However, if all the hinges were printed with the same grayscale (e.g., G20), all the hinges recovered their shape simultaneously at the same speed. This led to the collision of the panels and the failure of shape recovery (fig. S8).

We further exploited sequential SMPs for a robotic arm. As shown in Fig. 3C, the hand and elbow of the arm were designed with different $T_g$s using G80 and G20 for printing, respectively. The programmed temporary shape of the printed artificial arm showed sequential shape recovery at the same temperature: The hand (lower $T_g$) recovered first, and then the elbow (higher $T_g$) recovered (Fig. 3D). The sequential recovery of this arm was used in soft robotics. Figure 3E shows a robot programmed with an opening hand, and the arm has the capability to grab a long stick first and then bend the elbow to lift the stick (movie S6). The shape memory effect of the g-DLP–printed graded material can be further used for 4D printing by using the printed active composite (PAC).
We demonstrated that the g-DLP can be used to print composites with tunable mechanical properties (fig. S9). For example, a grayscale pattern with bright lines (G50) in the gray background (G85) was used to print a "fiber-reinforced composite with a fiber loading ($v_f$) of 33%. The fiber orientation has a strong effect on the modulus of the composite, which was verified by the theoretical estimation (35). Figure 3F shows a two-layer laminate composite, with one layer being a lamina with fiber (G50) in the matrix material (G85) and the other layer being the pure matrix material (G85). The printed composite experienced shape shifting by cold drawing due to the mismatch of strain recovery; this shifted shape can recover after heating (37). The bending angle of the PAC increased with unrecovered strain after stretching, which was affected by the applied strain (fig. S9). A larger film with asymmetric fiber distribution on two sides was also designed. After stretching and unloading at room temperature, the flat laminate shifted to a complex, nonuniform curvature (Fig. 3G).
Encryption via diffusion-assisted coloring

The different modulus and $T_g$ of the graded materials also lead to different diffusivity. The grayscale-dependent diffusivity can thus be used to visualize the grayscale pattern. For example, a continuous gradient grayscale pattern was used to fabricate a circular film with continuous mechanical property gradients (Fig. 4A). After immersing in a fluorescent/acetone solution followed by washing and drying, the center of a high grayscale region was visible under UV light (Fig. 4B). In addition, a cyan dye was used to make the grayscale pattern visible under sunlight. Figure 4C shows the dying kinetics monitored by tracking the intensity of red value (RGB color). The colored region was observed at the center and expands with time as indicated by decreasing red value (Fig. 4D). The colored region has a sharp boundary due to the nonlinear relationship between the grayscale value and diffusivity. Similarly, a circular pattern with concentric circles using alternating G20 and G80 was designed and printed (Fig. 4E). The pattern structure was visualized using both dye and fluorescein. The position-dependent color was also evaluated. For example, the sample colored by dye shows step variation in red value reflecting the discrete grayscale pattern used for printing (Fig. 4F). A similar step variation in green value was observed for the sample colored with fluorescein under UV light (Fig. 4G). This coloring using fluorescein shows application potentials for encryption and anti-counterfeiting. For example, a QR code was incorporated into a film by using the grayscale pattern for printing followed by treating with fluorescein solution. The pattern was not obvious under visible light; however, it can be "read" by UV light (Fig. 4H). Similarly, in Fig. 4I, a name card was designed to print a film followed by coloring a black dye. The QR code duplicated on the film can transfer to the inventory of "George P. Burdell" in Wikipedia by a smartphone (movie S7).

DISCUSSION

We report the g-DLP 3D printing assisted by two-stage curing to achieve high-resolution digital manufacturing of parts with complex shapes and programmable functional gradients. This two-stage curing strategy can be extended to other resin systems with the same concept of chemistry. For example, the replacement of diamine to multifunctional amine in the hybrid inks would be expected to generate a larger difference in cross-linking density after a two-stage cure. Acrylate oligomers with longer and flexible backbones can be used to enhance the stretchability of the graded materials.

The widely tunable mechanical gradients produced by g-DLP give rise to new combinations of functional properties for 3D printing. This new g-DLP technique serves as a platform technology for graded materials with tailor-made material properties and geometry complexity without (or with little) support materials. We showed that complex
2D/3D lattices with controlled buckling and well-controlled deformation sequence metamaterials with negative Passion’s ratio can be directly fabricated. In addition, the marked difference in mechanical properties can enable broader applications of direct 3D printed metamaterials, such as metamaterials with tunable acoustic band gap (38). Some other promising applications, such as organ models with stiffness variations, composites for 4D printing, and anti-counterfeiting, are also achieved. It should be mentioned that the g-DPL technique would provide a powerful tool for biomimetic graded material 3D printing. The duplication and investigation of gradient design in biological materials using this technique would deepen understanding of natural designs and provide some guide to fabricate high-performance structures. The new g-DLP method, thus, creates the possibility for future applications such as voxel printing and 4D printing for metamaterials (39, 40), presurgical model planning (33), soft robotics, and additive manufacturing with cyber security (41).

Although our approach enables significant advantages, there are still several issues that need to be addressed for its wide applications. First, the actual resolution of properties for the g-DLP should be determined. Besides the printer device itself, the voxel resolution for g-DLP in the x-y plane and z axis can be affected by both the resin and the printing parameters. Moreover, the grayscale value of the pixel would also have an influence on the voxel resolution. Second, the relationship between the curing condition, molecular structures, and mechanical properties of the grayscale cured samples needs to be further understood. The nanoscale mechanical test and modeling approaches would provide an attractive pathway to this end, which is part of the ongoing work. Last, when grayscale is used, polymers are cured to different degrees, which results in a slight difference in printed size. However, this can be fixed by software. For example, the projecting area with larger grayscale can be adjusted larger to compensate for the difference.

**MATERIALS AND METHODS**

**Ink preparation**

BPADA ($M_n = 468$), GMA, and BA with the weight ratio of 69:23:8 or molar ratio of 40:44:16 were mixed first. Then, 0.7 weight % (wt %)
Design and printing procedures by vat photopolymerization
3D printing was performed using a homemade DLP 3D printer. An oxygen-permeable window made of Teflon AF-2400 (Biogeneral Inc., San Diego, CA) was attached to the bottom of the resin vat. A PRO4500 UV-LED (Wintech Digital Systems Technology Corp., Carlsbad, CA) was used as the light source (385 nm). The projector light intensity was measured by an ILT1400-A Radiometer Photometer (International Light Technologies Inc., Peabody, MA). CAD files of the print part were designed in SolidWorks (Dassault Systèmes, Waltham, MA). The resulting STL files were sliced for a 2D file output by Creation Workshop software (DaraTree3D, Dallas, TX) using a slicing thickness of 60 μm. A voxel discrete grayscale pattern was generated with MATLAB (MathWorks Inc., Natick, MA) code developed in-house. More details about the grayscale can be found in the Supplementary Materials. Full-screen images with different grayscale patterns were projected onto the vat window for photopolymerization. The support plate was elevated by a motorized translation stage (MTS50-ZB, Thorlabs Ltd., Newton, NJ) mounted to a DC motor controller (TDC 001, Thorlabs Ltd., Newton, NJ). The printed layer thickness was 60 μm with printing time of 20 s for each layer. After printing, the parts were moved into a heating oven and cured at 70°C for 2 hours and another 10 hours at 120°C.

Characterization
Uniaxial tension tests were conducted on a universal material testing machine (Model Insight 10, MTS Inc., Eden Prairie, MN) with a load capacity of 10 kN and a cross-head speed of 1 mm/min at 25°C. At least three tests were conducted for each sample to get average results. The thermomechanical properties were measured on a dynamic mechanical analysis tester (Q800, TA Instruments, New Castle, DE) with a frequency of 1 Hz. The gel fraction was measured by soaking the samples in refluxing acetone at 70°C for 12 hours, followed by drying at 80°C for 6 hours. FTIR spectra ( Nicolet i50 spectrometer, Thermo Fisher Scientific, Waltham, MA) were recorded by averaging 32 scans of the signal at a resolution of 2 cm⁻¹ in attenuated total reflectance mode. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker Avance III 400 ( Billerica, MA) at ambient temperature in CDCl₃.

Encryption via diffusion-assisted coloring
The film samples were cured by shining grayscale pattern light on the hybrid resin sandwiched between glass slides for 20 s and then using the same thermal curing conditions. The thickness of the films was defined by plastic spacers (with thickness of 0.1 to 0.3 mm). The coloring process was conducted by immersing the film sample in dye or fluorescein solution for different times. The fluorescein solution contained 0.15 wt % of fluorescein (Sigma-Aldrich, St. Louis, MO) in acetone. The dye solution contained 10 to 15 wt % of cyan or black color ink (Hewlett-Packard (HP), Palo Alto, CA) in acetone/isopropanol alcohol (1/5, w/w). The coloring process using the dye took about 2 to 3 hours for film, and the encryption in fluorescein solution took only 10 to 20 s. Afterward, the samples were washed with isopropanol alcohol several times followed by drying. The fluorescein-treated samples were observed under a UV lamp (OmniCure S2000, Excitell Technologies Corp., Waltham, MA) with a 320- to 390-nm filter. All the colored samples were recorded by a digital camera, and the color was analyzed by ImageJ using the Color Profiler tool.

Finite element modeling
To investigate the local strains and stress on the deformed 3D structures with mechanical gradient, the finite element simulations were performed using a commercial FEA software ABAQUS (Simulia, Providence, RI). For the simulations in Fig. 1 (F and G), the bottom edge of the structures was fixed. The external load was applied by using pressure. The geometries were meshed using four-node linear quadrilateral elements with incompatible modes (CPS4H) for all the elastomeric components of the printed structures. For the simulation of the lattice graded material in Fig. 2 (A and B), the bottom surface of the structure was fixed, and the compression displacement was applied from the top surface. The linear elasticity model was used to represent the material constitutive behavior.

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/5/eaav5790/DC1
Supplementary Text
Fig. S1. Photopolymerization of acrylate and thermal curing reactions in the hybrid resin.
Fig. S2. Model reaction using a stoichiometric mixture of GMA and D230 by FTIR.
Fig. S3. Model reaction kinetics by ¹H NMR.
Fig. S4. Compression of 2D lattice metamaterial.
Fig. S5. Grayscale-dependent thermomechanical properties of g-DLP printed samples.
Fig. S6. Soft robotics by sequential SMPs.
Fig. S7. Grayscale-dependent thermomechanical properties of g-DLP printed after the first and second curing stages.
Fig. S8. Helical SMP component without recovery sequence.

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Sci Adv 5 (5), eaav5790.
DOI: 10.1126/sciadv.aav5790

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