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Submitted date: 15/05/2020 • Posted date: 18/05/2020
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Citation information: Deore, Bhavana; Sampson, Kathleen L.; Lacelle, Thomas; Kredentser, Nathan; Lefebvre, Jacques; Young, Luke Steven; et al. (2020): Direct Printing of Functional 3D Objects Using Polymerization-Induced Phase Separation. ChemRxiv. Preprint.
https://doi.org/10.26434/chemrxiv.12315488.v1

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Direct Printing of Functional 3D Objects Using Polymerization-Induced Phase Separation

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Abstract

3D printing has enabled the unique combination of structures, geometries and functional properties otherwise unattainable via traditional manufacturing techniques, yet its adoption as a mainstream manufacturing platform for functional objects is hindered by the physical challenges in printing of multiple materials. Vat polymerization offers a polymer chemistry-based approach to generating smart objects, in which phase separation is controlled in order to achieve, at once, desirable chemical and functional properties of final 3D printed objects, and indeed direct-production of 3D printed smart objects. This study demonstrates how the spatial distribution of different material phases can be modulated by controlling the kinetics of gelation, polymer network density and material diffusivity through the judicious selection of photoresin components. A rich selection of morphologies and functional coatings are generated, illustrating a promising way forward in the integration of dissimilar materials in 3D printed smart or functional objects.
Strategies to seamlessly integrate multiple materials into objects using 3D printing will enable the generation of new or improved material properties and advance 3D printing as a mainstream approach to manufacture functional and smart objects.\textsuperscript{1–14} Using reactive precursors, vat polymerization 3D printing provides a unique opportunity to spatially control materials from the surface to deep within the object.\textsuperscript{7,8,12,14–17} For instance, the spatial, temporal, chromatic and intensity characteristics of light have been used in vat polymerization to pattern material properties. Elegant examples include 3D printing using two wavelengths and orthogonal chemistries to spatially control polymerization,\textsuperscript{13} light intensity and oxygen inhibition to modulate the crosslinking density\textsuperscript{17} and photochromic molecules in combination with two wavelengths to control polymerization resulting in bioinspired materials of soft and hard sections.\textsuperscript{18} Moore and Barbera have recently demonstrated the demixing of precursors to yield bicontinuous phases of polymer and pre-ceramic precursor with domain sizes controlled by light intensity.\textsuperscript{12} Light-based printing techniques have also been used to photo-reduce \textit{in situ} silver precursors yielding silver nanoparticles during the printing process.\textsuperscript{19–23}

Here, we demonstrate that by using purposely formulated resins, material phases can be controlled within objects using vat polymerization. The method utilizes polymerization-induced phase separation (PIPS), a process previously used to generate 2D patterns in holographic polymerization.\textsuperscript{24–29} Exploiting concomitant changes in the thermodynamics of mixing that occur during polymerization, as well as spatio-temporal variations in monomer to polymer conversion, materials can be spatially directed towards the surface of the 3D printed object. The flux of functional material towards the surface of the printed object is controlled by balancing the kinetics of gelation, crosslinking density and rates of diffusion of the resin components. This approach has the benefit of generating material domains on the nanoscale and, thus, provides a
means to combine macro- and micron-scale 3D designs with nanoscale material phases, features not easily achieved with nanoscale printing approaches such as two photon polymerization, localized electroplating or metal ion reduction.

This report is the first to explore how resin formulation influences PIPS in vat polymerization (3D PIPS) and provides the insight needed to control material placement in printed objects. The use of 3D PIPS to spatially control material phases within printed objects opens up new opportunities to create functional coatings directly from printing or to generate material gradients that are essential to reduce stresses of integrating dissimilar materials. We demonstrate the utility of the approach by producing conductive metallic silver features, enabling the fabrication of a dipole antenna array, strain sensors as well as antibacterial surfaces. Using the principles described herein, this new freedom to design material complexity directly into 3D printed objects can be envisioned for generating complexes surfaces for 3D catalysis, improving the wettability of biocompatible resins with hydroxyapatite particles, or embedding anti-viral agents to minimize the transmission of pathogenic viruses in medical tools and devices and will pave the way to new technologies in structural electronics, shape responsive parts for soft robotics, as well as smart objects with embedded sensors for Internet of Things and wearables.

Crosslinkers drive the spatial distribution of silver

Here, we showcase a range of material morphologies that can be generated using photoresins containing a silver precursor as the non-polymerizable functional component (Figure 1). The silver precursor, silver neodecanoate (AgND), is ideal for this application as its molecular nature ensures higher diffusivity than larger functional materials such as nano- or microparticles. Furthermore, because AgND does not scatter light as particles do, resins containing high concentrations of the complex can be printed yielding highly conductive,
metallic silver surfaces through a simple post printing sintering step. The resin systems studied herein were comprised of varying concentrations of polyethylene glycol (PEG) diacrylate crosslinkers and a monomer, 2-ethylhexyl acrylate (EHA, Supplementary Table 1). The four resin systems, distinguished by the length of the PEG spacer of the diacrylates, formed the basis of this study (170, 250, 575 and 700 g/mol M<sub>n</sub> PEG-diacylates are referred to as DA-170, DA-250, DA-575 and DA-700, respectively; Supplementary Table 2).

By adjusting the resin composition, it is possible to tune the morphology of the printed part from one where silver is concentrated at the surface forming a distinct coating to one in which the silver is dispersed throughout the object. A high concentration of silver at the surface of the printed object necessitates that the AgND migrates to the surface before becoming entrapped in the polymer network; this occurs when the kinetics of gelation are slow, and when the diffusion of AgND is not inhibited by the formation of a tight polymer network. A composite morphology, where the concentration of silver varies minimally throughout the 3D printed object occurs when the kinetics of gelation are fast and the AgND is impeded from migrating as a result of a tight polymer network. By dialing-in conditions with intermediate rates of gelation and crosslinking densities, gradients in silver concentration can be achieved as the AgND diffuses controllably away from the locus of polymerization and towards the surface of the object.

3D PIPS was first demonstrated by printing cylinders 1.5 mm in diameter and 2 cm in length and sintered at 210 °C to convert AgND into metallic silver. The morphologies formed by the various resins can be seen in the SEM images taken at the edge of the cross-sections of the cylinders (Figure 2a). The images reveal that silver accumulates towards the surface of the object with some resins forming a defined silver layer or coating (e.g. 25 wt % DA-170) while others produce a graded composition in silver (e.g. 99 wt % DA-700). These morphologies were
assessed by performing 15 μm line scans at the edge of the cross-sections of the cylinders using Energy Dispersive X-ray Spectroscopy (EDS, Figure 2b). With the exception of two of the DA-170 resins (50 wt % and 99 wt % crosslinker), all cross-sections show that the concentration of silver increases from the core to the surface of the cylinder (Supplementary Figure 1). It should be noted that SEM images of the interface of un-sintered cylinders showed silver present at the surface demonstrating phase separation occurs prior to the sintering step (Supplementary Figure 2 and 3). All four series have similar behaviors; the lower the crosslinker concentration, the more the silver concentrates at the surface to form a silver coating. However, resins made with diacrylates with long PEG segments show more of a graded distribution in the silver at the surface. To more easily compare among resin systems, the surfaces of the cylinders were analyzed by EDS to give the wt % Ag within the first ~2 μm of the object as shown in Figure 2c. These results illustrate that for all resin systems, the amount of Ag that accumulates at the surface decreases with increasing concentration of crosslinker, in agreement with the analysis of the cross-sections of the cylinders. These results also show that the short diacrylates yield structures with a broader concentration range of surface silver than resins made with the long diacrylates. For instance, the Ag surface concentration varies from 88 % to 18 % for the DA-170 system, but only 86 % to 40 % for the DA-700 system when the crosslinker concentration increases from 25 to 99 wt %. These results demonstrate that the spatial distribution of silver in the printed object is dictated by the length of the diacrylate crosslinker and its concentration.

In most printed samples, the silver concentration at the surface is sufficient to form a conductive film once sintered. The electrical resistances of the cylinder as a function of wt % crosslinker of the resin (Figure 2d) shows that for all systems, the resistances increase with increasing fraction of crosslinker, in agreement with Figure 2c showing decreasing surface silver
with increasing wt % crosslinker. When the crosslinker concentrations are low, silver forms a coating with low resistance, owing to the high concentration of silver at the surface. As the crosslinker fraction increases, the coating progressively contains less silver, thus, increasing its electrical resistance. Above a certain fraction of crosslinker, the surface silver is below its percolation threshold resulting in no detectable electrical conductivity. The relative change in the resistance with increasing crosslinker lengths also agrees with the trend in surface silver; the resistance of cylinders made with short diacrylates increases more dramatically than with the longer diacrylates in concurrence with the more significant decrease in surface silver for the short diacrylates. These results demonstrate that 3D PIPS is a simple, single-step method to generate functional coatings on 3D objects and, thus, circumvents the disadvantages of two-step coating methodologies such as poor film adhesion and uniformity (see Supplementary Figure 4 for comparison).

**Gelation rate, crosslinking density and diffusivity**

With the aim to resolve differences in the behaviours of the various resin systems and to develop a predictive model for 3D PIPS, we examined how the crosslinker influences the diffusion of the AgND during phase separation. Diffusion of phase separating components, such as AgND, is influenced by the rate a homogeneous resin mixture is transformed into an insoluble gel. This rate determines whether the AgND becomes trapped by the network or diffuses freely towards the unreacted resin where mixing is more favourable due to entropic gains. We measured the time required for a resin to form a gel, or delay time ($t_d$), by detecting changes in the refractive index when a resin converts from monomer to a polymer network using phase contrast optical microscopy (Figure 3a and see Supplementary Videos 1-3). The $t_d$ values for the resin systems (containing no AgND) are summarized in Figure 3b and, as expected, $t_d$ decreases
with increasing wt % crosslinker. For instance, a resin containing 15 wt % DA-170 possesses an average $t_d$ of 5.8 seconds, while a resin composed of 99 wt % DA-170 has an average $t_d$ of 1.8 seconds. Moreover, for a given wt % crosslinker, the delay times decrease with increasing molecular weight (MW) of the crosslinker. This behavior likely results from the free end of long crosslinkers extending further from the polymer backbone, thus, increasing the probability of finding an unreacted acrylate group.\textsuperscript{39} We note that experiments performed using photoresins with AgND show similar trends in $t_d$ as a function of wt % of crosslinker (see Supplementary Figure 5). Figure 3c shows how the delay times correlate to wt % surface Ag; the longer the delay time, the greater the amount of surface silver. Therefore, resins that remain homogeneous mixtures of polymer, monomer and crosslinker for a longer duration afford more time of unimpeded migration for the AgND to reach the surface of the object.

Although Figure 3c highlights how the delay time affects surface morphology, the results reveal that the resin systems generate different amounts of surface Ag for a given delay time, indicating that the amount of Ag that reaches the surface is not solely dictated by gelation rates. The effect is particularly pronounced at low delay times (\textit{i.e.} high crosslinker concentrations) where resins made with long diacrylates yield objects with higher concentrations of surface silver than shorter diacrylates. We considered the role of miscibility between the AgND and the resin by comparing their calculated solubility parameters, $\delta$ (see Supplementary Table 1 and Supplementary Figure 6). However, for a given wt % crosslinker, the differences in solubility parameters for the different systems is marginal and do not explain the behavior highlighted in Figure 3c.

The diffusivity of AgND will impact the amount of Ag that accumulates at the surface and may explain the observed differences in surface silver for a given delay time. The diffusivity
of AgND will change during polymerization as a result of increases in viscosity and constraints imparted by the growing polymer network. The extent to which the diffusivity of AgND will change when the resin is transformed into a polymer network will be highly dependent on the length of the spacer between reactive moieties in the crosslinker. To explore this idea, coarse-grained Langevin dynamics simulations of a simplified system were performed (see Methods for details). The simulations tracked the displacement of a probe molecule, representing AgND, in a dense ensemble of crosslinker molecules (100 wt % crosslinker) of varying lengths. The simulations examined the diffusivity of AgND in two cases: unreacted resin and a fully formed polymer network.

The diffusion coefficient of the probe molecule in crosslinkers of different lengths (L=3, 6 and 9) is shown in Figure 4a. In the absence of any polymerization, the diffusion coefficient is higher in the short crosslinker. This is to be expected as the viscosity of the solution increases with increasing MW. However, for the case of diffusion in the polymer networks, the diffusion coefficient is highest for the longest crosslinker. In this limit, the networks formed by the shorter crosslinkers have a higher density of crosslinking points and, correspondingly, smaller pore sizes. This can be seen by examining the images for the probe molecule in the L=3 network (Figure 4b) and in the L=9 network (Figure 4c). Long linear bridging segments are essentially absent in the L=3 network, but are apparent in the L=9 network as they correspond to the crosslinkers themselves. Note that the y-axis in Figure 4a is logarithmic and, thus, the decrease in diffusivity for the short crosslinkers is much more dramatic than for the long crosslinkers. The diffusion of the probe molecule is ~24 times greater in the unreacted resin than in the network for L=3, but it is only ~2 times greater for L=9.
The inset to Figure 4a shows the diffusion coefficient of the probe molecule in the polymer networks as a function of crosslinker length. Of note, the diffusion coefficient for the probe molecule is larger in the L=9 network than the L=3 network outside of the error bars. This inversion could be heightened in the experiments due to the ratio between long and short crosslinkers being higher (see Methods). However, the simulations do clearly indicate that the diffusivity of AgND is very likely to be lower in the polymer network made with a tight crosslinked network. Reduced diffusivity in the tight network formed by short crosslinkers will impede the ability of AgND to migrate to the surface and, thus, provide a rationale for the lower surface Ag found in the system with shorter crosslinkers at low delay times. These results show how the interplay between the rate of network formation and the temporal changes in diffusivity of AgND that occur during polymerization affect the extent to which AgND migrates to the surface, which ultimately dictate the spatial distribution of silver in the object.

3D PIPS for smart objects

Using purposefully formulated resins to control the placement of AgND, we demonstrate the value in being able to tune the surface morphology of printed objects with particular material properties by considering three applications: strain sensors, antennas and antimicrobial objects. The 3D PIPS approach provides the ability to generate strain sensors with complicated 3D geometry and holds promise in wearable electronics and motion sensing. Truss structures were 3D printed to using a resin formulation that yields graded silver compositions. As these formulations yield thermosets with low stiffness, it is possible to compress the objects and modify the electrical resistances based on the applied compression. The SEM images of the surfaces and cross-sections of strain sensors in Figure 5a reveal that as the wt % crosslinker used in the resin increases, Ag particles forming the surface coating become progressively sparser.
with more polymer inclusions in between the silver particles. The differences in morphologies lead to different electrical responses under applied compression (Figure 5c). For the truss made with 39 wt% crosslinker, the surface features a dense film of Ag nanoparticles with low electrical resistance whereas the truss made with 58 wt% crosslinker has a surface morphology with sparser particles and, correspondingly, higher electrical resistance (Supplementary Figure 7). As shown in Figure 5b, compression increases the number of particle-to-particle contacts, consequently increasing the pathway for electrical conduction; this is proportionally larger for the truss that has sparser surface Ag than the truss that has a dense film of Ag nanoparticles. As a result, the change in resistance upon compression is greater for the truss made from resins with high crosslinker concentration. These examples show the power of 3D PIPS to generate strain sensors of variable electrical responses under compression by tuning the resin composition.

3D printing is ideally suited to fabricate millimeter wave antennas for 5G as 5G will function on small networking cells that use arrays of antennas in small geographical areas requiring a large number of integrated low lost devices. These requirements can be achieved by using 3D printing to make antennas low cost, in arrays and embedded in objects. Moreover, by suspending the antenna in air using a 3D design, signal loss can be minimized with air becoming the effective dielectric. Using the 3D PIPS approach, we fabricated an array of 3D printed dipole antennas and demonstrated transmission of 2.4 GHz waves. The dipole antenna array, shown in Figure 6a, displays the radiation pattern found in Figure 6c as measured using an anechoic chamber (Figure 6b) and its comparison with the theoretical response for a dipole array on a ground plane. The focusing of the radiation pattern into a main lobe is the result of radiation interference between antenna elements. The half power beam width of the theoretical pattern is
48° compared to 45° for the measured pattern, resulting in a remarkably small difference of 3° and, thus, demonstrating the suitability of this printing process for antenna applications.

Antibacterial properties of nanoparticle silver have been used in many medical and dental applications for the prevention of infection.42–44 To evaluate the antibacterial behaviors of 3D printed Ag objects, a halo inhibition zone test against E.coli as well as bacterial growth kinetics were carried out along with control objects containing no silver. A concentration of 0.5 or 1.0 wt % Ag was used in this study in order to form Ag nanoparticles rather than a film on the surface (Supplementary Figure 8). As seen in Supplementary Figure 9, the 3D objects containing Ag show a bacterial inhibition zone on agar plate and bacterial inhibition in the liquid medium of E.coli while the control samples show growth of E. coli. These results demonstrate the antibacterial properties of 3D printed Ag objects and illustrate how 3D PIPS could provide a means to embed small quantities of antimicrobial or antiviral agents at surfaces of printed objects helping to minimize the transmission of pathogenic bacteria and viruses.

The concept of 3D PIPS can be applied broadly to fabricate 3D objects with different surface properties by using various functional materials with resins that induce migration of these materials towards the surface. 3D PIPS was used to generate 3D objects with various surface composition, as illustrated in the examples of Supplementary Figure 10 that use resins loaded with nanoparticles.

In summary, we have showcased how the temporal and spatial variation in monomer-to-polymer conversion that takes place in vat 3D polymerization causes local demixing of functional materials, triggering diffusion of these materials towards the bulk resin. By harnessing the rate at which the functional materials become entrapped in the polymer network during 3D PIPS, a wide range of surface morphologies can be accessed. The insight gained in controlling
the material phases allows a rationalized approach to formulating resins to access a wide range of material morphologies for specific applications. Due to the universality of this approach, 3D PIPS represents a powerful method to create materials with controlled sub-phases and will accelerate the adoption of vat polymerization as a viable technique to generate functional 3D objects.

Methods

3D Printing Functional Photo-Resin Preparation: Photoresin Preparation: Components used to make photoresins are shown in Supplementary Table 1. Acrylate photoresins were prepared by varying the amount of monomer and crosslinker ranging from 15 wt % to 99 wt % crosslinker with 1 wt % photoinitiator and the remaining wt % monomer as shown in Supplementary Table 2. The combined mixture was vortex mixed for 30 s before use. Photoresin with AgND: The silver precursor, referred to as AgND, was prepared by mixing 2.5 g of silver neodecanoate in 0.55 mL of 2-ethyl-2-oxazoline (1:0.6 mole ratio) using a planetary mixer at 2000 rpm for 4 min followed by 2200 rpm for 30 seconds resulting in an 82 wt % of silver neodecanoate in 2-ethyl-2-oxazoline. To make resins loaded with silver precursor, 3.0 g of AgND was added to 9.2 g of photoresins yielding compositions containing 25 wt % of AgND. These resin formulations are comprised of 8.0 wt % of silver metal or 9.5 wt % silver metal post-sintering assuming neodecanoate and 2-ethyl-oxazoline become volatile during the process. Although resins containing up to 50 wt % of AgND could be used to print objects, resins with 25 wt % AgND were used unless otherwise stated. Measurable electrical conductivity was observed for resins containing >15.8 wt % AgND. The resistance of the surface of the cylinders did not change significantly when the concentration of AgND in the resin was > 25 wt % while AgND amounts greater than 38.2 wt % reduced the printing ability and strength of the objects. Resin
Preparation for Strain Sensor: Mixed DA-resins were prepared by mixing different volumes of two separately prepared DA-resins such as 75 mL of DA-575 resin (40 – 65 wt % DA-575) with 25 mL of a 35 wt % DA-250 resin to vary the total amount of crosslinker between 39-58 wt %. To make functional resin, 3.0 g of Ag precursor was then added to 9.2 g of mixed DA-resin to adjust the amount of Ag metal in the resin to 8.0 wt %. The combined mixture was then vortex mixed and used to print truss structures used as the strain sensors. Resin Preparation for Dipole Antennas: Resin mixtures were prepared by mixing different volumes of two separately prepared DA-resins, namely, 75 mL of 50 wt % DA-575 with 25 mL of 35 wt % DA-250. 3.0 g of Ag precursor was then added to 9.2 g of mixed DA-resin to adjust the amount of Ag metal in the resin to 8.0 wt %. The combined mixture was then vortex mixed and used to print dipole antennas. Preparation of Dipole Antenna by Electroless Silver Plating: The mixed DA-resins were prepared by mixing different volumes of two separately prepared DA-resins such as 75 mL of 50 wt % DA-575 and 25 mL of 35 wt % DA-250. The dipole antennas were then printed without a silver precursor and then coated with silver by modifying a previously reported electroless-plating method. The electroless silver plating bath was composed of solution A (0.2 g of glucose, 0.02 g of tartaric acid and 0.5 mL of ethanol in 20 mL of deionized water) and solution B, a Ag(NH₃)²⁺ solution (0.2 g of AgNO₃, 0.075 g of NaOH and 0.5 mL of ammonia in 20 mL of deionized water). These two solutions were mixed by dropwise addition of Ag(NH₃)²⁺ solution B into solution A bath containing dipole antennas at room temperature with constant stirring over the period of 60 minutes. After reacting for 60 min, the antennas were collected, rinsed with water and dried at 140 °C for 5 minutes. Functional Resin Preparation for Antibacterial Activity: 3D objects for antibacterial activity measurements were prepared using 0.0 to 1.0 wt % of Ag metal in 35 wt % DA-575 resin.
Printing, Sintering and Characterization of 3D Objects: **SLA Printing of 3D Objects:** 3D objects using functional material were printed using Peopoly Moai Laser SLA 3D Printer (Technical Specifications: Build Volume: 130 x 130 x 180 mm, Laser spot size: 70 microns, Laser wave length: 405 nm, Laser power: 150 mW (measured power output 30 mW), Machine size: 330 x 340 x 660 mm, Layer Height: 10 – 200 microns, Z resolution: Layer Height: 10 – 200 µm). Objects were printed using a fluorinated ethylene propylene-liner-coated vat with laser power rating set to 75 and all other setting set to the default. **Sintering of Printed 3D Objects:** 3D objects were thermally sintered on a Kapton sheet at ~210°C (substrate temperature) for an hour using a reflow oven under nitrogen with 500 ppm oxygen. **Characterization of 3D Objects:** The resistance of the 3D printed objects per cm of cylinder was measured using a digital multimeter after thermal sintering. Scanning electron microscopy (SEM) imaging and Electron Dispersive X-ray Spectroscopy (EDS) surface and cross-section analysis were performed with a Hitachi SU3500 using acceleration voltage of 15 kV (SEM) and 30 kV (EDS) and spot size of 30. **Optical Studies of Resin (Polymerization Kinetics):** The photopolymerization was studied in an experiment separate from printing using an optical microscope to observe the changes in refractive index which occurs as the resin was converted from monomers/crosslinkers to polymer under illumination by a 405 nm laser as shown in Supplementary Figure 11. Each resin was prepared in 2 – 10 mL quantities (see Supplementary Table 2 for formulations) and loaded into a capillary micro glass slide (0.10 x 2.0 mm, 0.10 mm wall thickness; Electron Microscopy Sciences). The filled capillary micro glass slide was placed under the optical microscope (Nikon ME600) fitted with a 405 nm laser and optical filters (405 nm laser line and 405 nm Raman edge filters) to prevent saturation of the camera with unwanted laser light. Laser power (10 µW with 1-2 µm diameter spot size) was set low enough to reveal polymerization in a 10 – 60 s timescale.
Refractive index changes can be best visualized using phase-contrast imaging mode. Videos were acquired by a color camera (Luminera Infinity2) and include an initial phase without laser illumination, followed by removal of a laser shutter where resin/crosslinker exposure is initiated. A small dot is observed after a few seconds which subsequently grows to an island several micrometers in diameter (200 – 400 µm). The shutter is closed and recording stopped once the island stopped growing (see Supplementary video 1-3). Each recorded video was subsequently analyzed with ImageJ. For a polymerized island, a slice through the center was selected to construct a plot of the island size as a function of time (Supplementary video 3). The start time was accurately determined from the slight change of illumination conditions when the shutter was On or Off. The two opposite edges of an island and their time evolution can be clearly identified and fitted to Equation (1):

$$\text{Profile} = \pm \left( D_f - D_f e^{-\sqrt{|t_t-t_d|/t_c}} \right)$$

where \( t_d \) is the delay time, \( t_c \) is a rate dependent parameter, and \( D_f \) is a size dependent parameter. The \( t_d \), which represents the time elapsed between when the laser is turned on and the first observable sign of polymer network, serves as a measure of relative gelation time. This was repeated two more times with newly filled capillary tubes for each formulation measured.

**Coarse-grain modeling of the diffusivity of a probe molecule:** The simulations used standard coarse-grained (CG) polymer methodologies\(^{46}\) to construct a system roughly modeled on the experimental setup. A cubic box was filled with CG polymers that represent the crosslinkers. Each polymer consists of L beads that are linearly joined together via FENE spring bonds\(^{47}\) to prevent bond crossing. Inter- and intramolecular interactions between beads were implemented using the WCA potential\(^{48}\) such that there is no attraction between beads, but instead there is only short ranged repulsion that yields excluded volume. Stiffness is imparted to each polymer
via a harmonic angle bond that causes a linear alignment of any three consecutive monomers to be the energetically favourable conformation. Each simulation also included a single probe molecule that represented one AgND molecule.

A length of L=3 beads was chosen to roughly correspond to the length of the DA-170 crosslinker. AgND, which is of similar length to DA-170, was also modeled as an L=3 molecule. Simulations were also performed for crosslinker molecules of length L=6 and L=9 to study how the dynamics change with crosslinker length. The L=9 molecule was the longest length that could be studied due to constraints on the simulation setup. Thus, these simulations do not replicate the crosslinker ratios studied experimentally and instead explore the dependence on crosslinker length in a more general way.

The diameter of each bead was set to $\sigma$ and, thus, $\sigma$ serves as the length scale for the simulation. The box length was set to 20 $\sigma$ and each system was filled with enough polymers to achieve a volume fraction of ~49%. This density is high enough to approximate the pure polymer melt of the experiments, but is also low enough to allow for the movement of individual crosslinker molecules on simulation time scales. This middle ground then mimics the experimental setup while permitting the exploration of the dynamics of the system. The systems then consisted of: 2500 L=3 crosslinkers + 1 L=3 probe molecules, 1250 L=6 crosslinkers + 1 L=3 probe molecule, and 833 L=9 crosslinkers + 1 L=3 probe molecules. Images from the L=3 and L=9 systems are shown in the Supplementary Figure 12.

For each crosslinker length, simulations were performed for two scenarios: diffusion of the probe molecules in pure resin (no polymerization of crosslinkers) and in the final network (saturated polymerization). For both scenarios, the system was evolved in time via Langevin dynamics\textsuperscript{46} using the HOOMD blue simulation packaged.\textsuperscript{49,50}

The setup of each system consisted of a number of preliminary steps. First, the box was filled with the specified number of polymers and one probe molecule being constructed on a
grid. Second, the system was randomized with a short simulation where there were no intermolecular interactions. This allows all molecules to pass through each other and, thus, randomizing the system very quickly. Third, the excluded volume interactions between beads on different molecules was ramped up until the full potential was applied. This method yielded the initial configurations shown in the Supplementary Figure 12.

For the simulations of diffusion in pure resin, these initial states were then evolved in time and the position of the probe molecule was monitored. The mean square displacement (MSD) of the probe molecule was then calculated from these trajectories by internal averaging. The diffusion coefficient was extracted from a linear fit of the MSD plotted against simulation time.

For the simulations of diffusion in the network, simulations were performed in two steps. In the first step, a polymer network was formed by setting 10% of the cross-linkers to be reactive allowing polymerization to take place via diffusion. These network formation simulations were conducted for a long enough time period that the rate of adding new crosslinking points became very small. The resulting networks were then considered fully polymerized. Once the network was formed, a second simulation was conducted in which the diffusion of the $L=3$ probe molecule representing AgND was monitored. No further polymerization occurred during this step.

Analysis of the MSD and resulting diffusion coefficient was conducted in the same manner as the pure resin case. However, there are more sources of variability in the network case since the network is not homogenous (while the pure resin essentially is). This means that the rate of diffusion depends on the local environment and, thus, varies as the probe explores different areas of the network. Further, since the simulations are limited in the size of the
network that is constructed, the results will also vary between different simulations. Even though
the simulations are identical in procedure, if a different seed is used to initiate the dynamics then
the network that is formed will be significantly different between simulations and, thus, the
calculated diffusion coefficient may also be significantly different.

To account for these variations, simulations were performed using three different initial
seeds to build three independent networks for each crosslinker length. The final diffusion
coefficient given in the main manuscript is the average of the value calculated for each
realization. The error bars correspond to the standard error as calculated across the ensemble of
three.

**Applications: Strain Sensor Measurements:** The 3D-printed truss objects (12 x 12 x 12 mm)
were affixed to a programmable linear stage (Zaber Technologies; model X-LRQ150AP-E01)
with aluminum tape and two-component silver epoxy (#8330S-21G, MG Chemicals) as shown in
Supplementary Figure 13. The stage was controlled using the LabVIEW software package and
changes in electrical resistance were measured using a digital multimeter (Keithley Integra Series
2701 Ethernet Multimeter/Data Acquisition System) with probes connected to the aluminum tape
spaced approximately 1.2 cm across from the sample. All samples were measured at a
compression/elongation rate of 625 μm/s in increments of 5 μm with a 1 s pause before each
resistance measurement.

**Dipole Antenna Measurements:** Dipole antennas were 3D printed using functional resin with
Ag precursor adjusted so that the amount of Ag metal in the resin was 8.0 wt %. A microstrip
array was used to feed four dipole antennas, which were metalized after 3D printing via phase
separation of Ag and post-printing sintering. The photograph of the antenna array is shown in
Figure 6a. The dipole antenna measurements were performed in an anechoic chamber (Figure
The antennas were designed to be centered at 2.4 GHz with a physical length of 6.25 cm. A gain standard horn antenna was positioned at one end of the chamber and connected to one port of a Vector Network Analyser (VNA) through an amplifier. The device under test (antenna array) was placed at the opposite end of the chamber on a rotating mount and connected to the other port of the VNA. While rotating the antenna array, s-parameter measurements were taken to determine the radiation of the antenna as a function of angle. Only the positive going half of the radiation pattern was used to determine the half power beam width. A signal present at angles between 90° and 270° were due to the finite limitation of the ground plane and the noise naturally present in the system.

**Antibacterial Activity: Halo Inhibition Zone Test:** Bacterial suspension TG1 (E.coli) at concentration of \(~ 1 \times 10^9\) colony-forming units (cfu)/mL was plated on LB agar plate and incubated for 18 h at 37 °C to detect the existence of the growth inhibition halo around the samples. **Bacterial Growth Kinetics Test:** To evaluate the bacterial growth kinetics in the liquid medium of E.coli, samples were placed in the diluted bacterial suspension at the concentration of \(10^5 \sim 10^6\) cfu/mL, which were subsequently cultured in a shaker incubator at 37 °C and 220 rpm. After predetermined times, the optical density, a measure of cell growth, was determined at 600 nm (OD600) using a microplate reader (Varioskan Flash, Thermo Scientific).

**Acknowledgements**

We thank Mary Foss for antibacterial studies, Douglas Moffatt for strain sensor experimental setup and Mary Gallerneault for dipole antenna SEM analysis and editing.

**Author contributions**
B.D. and C.P. conceived the idea together and designed the experiments. H.W.dH. devised and performed the simulations as well as interpreted results. K.L.S. acquired the gelation rates, T.L. fabricated and measured the response of the strain sensors, and J. L. designed and setup the \textit{in-situ} measurement of polymer network formation. The antenna measurements were performed by J. H. while the interpretation of the results were done by J.H. and R.E.A. T.J. performed the antimicrobial experiment. N.K and L.S.Y. printed, processed and characterized printed cylinders. Material characterization was performed by B.D., C.P., K.L.S. and T.L. The manuscript was co-written by B.D., C.P., K.L.S., T.L., J.L., J.H., H.W.dH., T.J. and P.R.L.M.

\textbf{Competing interests}

The authors have filed patent applications related to this work.

\textbf{Additional information:} Supporting information; Supplementary Table 1-2, Supplementary Figures 1-13 and videos 1-3.
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Figure 1. 3D PIPS printing mechanism of functional objects. a) Schematic of the phase separation of AgND induced by PIPS while 3D printing. b) Tuning of phase-separation by controlling crosslinking density to yield different morphologies in 3D objects. c) Photographs of PIPS induced 3D printed and sintered Ag coated objects.
Figure 2. Silver phase separation as a function of crosslinking density. a) Cross-sectional SEM images focussed approximately < 5 µm from the edge of the cylinder as pictured in Figure 1b. b) Weight fraction of silver as a function of depth with respect to the surface as measured by performing EDS on the surface of the object (data point at 1 µm) and on the cross-sections of the cylinders for 25, 50 and 99 wt % crosslinker of each DA type. c) Surface silver as a function of wt % crosslinker as measured by EDS analysis on the surface of the object. The estimated interaction volume of the EDS beam for these measurements performed on the top surface of the object is ~2 µm. d) Resistance as a function of wt % crosslinker.
Figure 3. Dynamical study of photoresins by optical microscopy and silver migration. a) Constructed images obtained from videos of islands of polymer formed when resin/crosslinker inside a capillary is exposed to a focussed 405 nm laser spot. A slice through the center of the island reveals its two opposite edges and is plotted as function of time. Two examples i) and ii) are shown for 15 wt % DA-170 and 99 wt % DA-700. b) Delay time, $t_d$, extracted from a fit to Equation 1 (See Supporting Information) for the resin formulations in this work, as a function of wt % crosslinker. c) Weight % of Ag extracted from SEM/EDS analysis at the surface of the cylinder as a function of $t_d$ for various resin formulations.
Figure 4. a) Diffusion coefficient of a probe molecule in crosslinkers of different lengths (N=3, 6 and 9) before and after the formation of a polymer network. The inset shows the diffusion coefficient of the probe molecule as a function of the crosslinker length in the formed network. Snapshots of the probe molecule in a network form with crosslinker b) N=3 and c) N=9.
Figure 5. Strain sensor measurements. a) SEM images of the top surface and cross-section of truss structures prepared using different wt % crosslinker. b) Schematic representation of compression mechanism within truss. c) Change in resistance measurements upon compression cycling of truss structures prepared with different wt % crosslinker. Trusses made with 39, 46 and 52 wt % crosslinker responded to a 250 μm compression with maximum changes in resistance of 2.5, 6.0 and 12.5%, respectively.
Figure 6. 3D printed dipole antenna array. a) Photograph of antenna array. b) Anechoic chamber layout. c) 3D printed dipole antenna array normalized radiation pattern at 2.4 GHz compared with ideal array factor.
Supporting Information

Direct Printing of Functional 3D Objects Using Polymerization-Induced Phase Separation

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Supplementary Figure 13: Experimental setup for the strain sensor measurement. The sample dimensions are 12 x 12 x 12 mm.

List of Videos

Supplementary Video 1: Optical microscope capture of polymer network island growth of 15 wt % DA-170 resin.

Supplementary Video 2: Optical microscope capture of polymer network island growth of 99 wt % DA-700 resin.

Supplementary Video 3: Optical microscope capture of polymer network island growth of 99 wt % DA-700 resin with laser on time and sliced area highlighted.
**Supplementary Table S1.** Resin Components and their Solubility Parameters.

| Structure | Name                                  | Molecular Weight (g/mol) | Solubility Parameter (MJ/m$^3$)$^{1/2}$ |
|-----------|---------------------------------------|--------------------------|------------------------------------------|
|           | **Crosslinker**                       |                          |                                          |
| ![Crosslinker](image) | DA-170                                | 170                      | 19.30                                    |
|           | DA-250                                | 250                      | 19.16                                    |
|           | DA-575                                | 575                      | 18.89                                    |
|           | DA-700                                | 700                      | 18.77                                    |
|           | **Monomer**                           |                          |                                          |
| ![Monomer](image) | 2-Ethylhexyl acrylate               |                          | 16.90                                    |
|           | **Photoinitiator**                    |                          |                                          |
| ![Photoinitiator](image) | Ethyl (2,4,6-trimethylbenzoyl) Phenylphosphinate | |                                           |
|           | **Non-Polymerizing Component**         |                          |                                          |
| ![Non-Polymerizing Component](image) | Silver Neodecanoate               |                          | 20.30*                                   |
| ![Non-Polymerizing Component](image) | 2-Ethyl-2-Oxazoline               |                          | 18.71                                    |

*Silver neodecanoate solubility parameter was estimated and calculated as neodecanoic acid*
Supplementary Table S2. Composition of Polymerizing Components of Photoresins.

| Crosslinking Density wt % | Monomer Ethylhexyl Acrylate (g) | Crosslinker DA* (g) | TPO-L Photoinitiator (g) | Total DA-resin* (g) |
|---------------------------|---------------------------------|---------------------|--------------------------|---------------------|
| 15                        | 8.4                             | 1.5                 | 0.1                      | 10                  |
| 20                        | 7.9                             | 2.0                 | 0.1                      | 10                  |
| 25                        | 7.4                             | 2.5                 | 0.1                      | 10                  |
| 35                        | 6.4                             | 3.5                 | 0.1                      | 10                  |
| 50                        | 4.9                             | 5.0                 | 0.1                      | 10                  |
| 60                        | 3.9                             | 6.0                 | 0.1                      | 10                  |
| 65                        | 3.4                             | 6.5                 | 0.1                      | 10                  |
| 80                        | 1.9                             | 8.0                 | 0.1                      | 10                  |
| 99                        | 0                               | 9.9                 | 0.1                      | 10                  |

*DA-resins DA-170 to DA-700 were prepared using crosslinkers DA-170 (EGDA), DA-250 (PEGDA250), DA-575 (PEGDA575) and DA-700 (PEGDA700).

It should be noted there exists a lower limit in the amount of crosslinker that can be used to promote 3D PIPS that is determined by practical printing requirements. We found that the printability of the objects begin to degrade substantially when resins contain less than 15 – 20 wt % crosslinker due to insufficient strength of the polymer to support the layer by layer growth of the printed object.
**Supplementary Figure 1.** The Ag wt % as a function of distance away from the surface along the cross-section of a 1.5 mm diameter cylinder. The center of the cylinders have as low as 4 wt % Ag.
Supplementary Figure 2. SEM images cross-sections of un-sintered cylinders printed using two different crosslinkers and after having undergone 5 minutes of UV curing to convert some of the silver salt to silver metal: (a, b) 25 wt % DA-170 and (c, d) 25 wt % DA-250. These results suggest that the silver complex diffuses to the surface during printing and the partitioning of material phases does not happen post-printing.
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**Supplementary Figure 5.** Delay time of DA-575 resin with and without Ag precursor as a function of wt % of crosslinker measured using the optical microscope setup.
Solubility Parameter

The solubility parameters (\(\delta\)) of monomers, crosslinkers and the silver complex were estimated using group contribution methods.\(^1\) From these values, the solubility parameters of the monomer/crosslinker mixtures of each resins were estimated by calculating a volume weighted solubility parameters. These values are plotted in Figure S6 and compared to the \(\delta\) value of the 2-ethyl-2-oxazoline and neodecanoic acid (purple and blue horizontal line, respectively).

![Solubility parameters graph](image)

**Supplementary Figure 6.** Solubility parameters of monomers, crosslinkers and the silver complex estimated using group contribution methods.

1. van Krevelen, D. W., Krevelen, D. W. & te Nijenhuis, K. *Properties of polymers: Their correlation with chemical structure; their numerical estimation and prediction from additive group contributions.* (Elsevier, 2009).
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