# Impact of PEGDA Photopolymerization in Micro-stereolithography on 3D Printed Hydrogel Structure and Swelling

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# **Supplementary Information**

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### S.I Experimental Setup for 3D printing of PEGDA hydrogel samples



**Fig. S1.** The working principle of the DLP-based SLA printer illustrating the 3D printing setup in (3) and the fabrication of a 3D printed PEGDA mini-Rook (Chess piece) in (4).

#### S.II Resin formulation

A photo-crosslinkable pre-polymer solution was prepared with Poly(ethylene glycol) diacrylate (PEGDA,  $M_n$  =575), diphenyl (2,4,6- trimethylbenzoyl)-phosphine oxide (TPO) as the photoinitiator (Sigma Aldrich), all purchased from Sigma Aldrich, USA. PEGDA is a long-chain, hydrophilic, and homobifunctional monomer. The TPO photo-initiator is added directly to PEGDA with 0.1%(w/w) concentration. The mixture is agitated on a magnetic stirrer at room temperature for 2 hours to fully dissolve the TPO. Note that no other solvents are added for purpose of comparing our experiment with the corresponding simulation except for results presented in Figure 5(a,b).

#### S.III Simulation details for polymerization and microstructure formation

#### S.III.I Reactive force field

To model the photo-polymerization process at the molecular-level, we carried out large-scale reactive coarse-grained simulations. It should be emphasized that the chemical bonds can form or break depending on the local atomic configuration as well as thermomechanical conditions spontaneously dictated by the reactive force field used, instead of relying on stochastic Monte-Carlo operations. Here we utilized an existing reactive force field, which has been used to investigate the difference of chain-growth polymerization in solution versus on surface. We kept the same force field formulation while adjusting some of the parameters to better mimic the photo-polymerization process. We also included additional particle species to achieve radical-polymerization, initiation, and termination. The details of reactive force field design can be found in Ref.<sup>1</sup> The formulation and parameterization of the force field used here will be described below.



**Fig. S2.** Schematic of various particles in our reactive coarse-grained model. The polymer chain is [-A-B-]. The initiator is I. Monomers are APA and BPB. Terminators are TAEA and TBEB. The chain-growth process is shown on the right pane, with the radical end marked by the star. The particle types are slightly different from Reference<sup>1</sup>.

There are nine species of coarse-grained particles in this model as shown in Figure S2. Particles A and B link alternatively and form the linear polymer chains [-A-B-]. As A and B particles have identical interaction to other species, with the only exception that both types of particles repel their own species. Therefore, polymer chains [-A-B-] most closely resemble polyethylene. Particles P bond to Particles A and B to prevent polymerization unless a radical particle (naked A or B particles, or the initiators) is involved. The initiator molecules are introduced to the system as molecule I. As particle I has only weak repulsion to particle A, particle I can bond to two chains thus serving as cross-linkers. Here, particles I serve the dual role of initiators and cross-linkers, which mirrors the dual role of TPO in our experiments. Terminator molecules are molecule T<sub>A</sub>E<sub>A</sub> (for terminating particles A) and T<sub>B</sub>E<sub>B</sub> (for terminating particles B).

The particle-particle interaction is described by a modified Lennard-Jones (mL) potential. The mL potential differs from the conventional  $\phi_{LJ}^{smooth}(r)$  by the inclusion of a repulsive bump term b(r) outside of the potential well. The pair-wise interaction of  $f_{mLJ}(r)$  can be written as,

$$\phi_{mLJ}(r) = \begin{cases} \phi_{LJ}^{smooth}(r), & r < r_{\alpha\beta}^{s} \\ \phi_{LJ}^{smooth}(r) + b(r), & r \ge r_{\alpha\beta}^{s} \\ 0, & r \ge r_{\alpha\beta}^{c} \end{cases}$$
(1)

where  $r_{\alpha\beta}^{c}$  is the species-dependent cutoff ( $\alpha$ , b denotes species of A, B, P<sub>A</sub>, P<sub>B</sub>, or T<sub>A</sub>, T<sub>B</sub>, E<sub>A</sub>, E<sub>B</sub>, and I). The bump term b(r) is only applied in the range of  $r_{\alpha\beta}^{s}$  and  $r_{\alpha\beta}^{c}$   $b(r) = e_{\alpha\beta}^{b}e_{AB} \cdot sin^{2}\left(\rho \frac{r_{\alpha\beta}^{c} - r}{r_{\alpha\beta}^{c} - r_{\alpha\beta}^{s}}\right)$ . To ensure the potential energy

and its first derivative is continuous at  $r_{\alpha\beta}^{c}$ , the original LJ potential is smoothed as follows:

$$\phi_{LJ}^{smooth}(r) = \phi_{LJ}(r) - \phi_{LJ}(r_{\alpha\beta}^{c}) - (r - r_{\alpha\beta}^{c})\phi_{LJ}'(r_{\alpha\beta}^{c})$$

$$\phi_{LJ}(r) = 4\varepsilon_{\alpha\beta} \left(\frac{\sigma_{\alpha\beta}^{12}}{r^{12}} - \frac{\sigma_{\alpha\beta}^{6}}{r^{6}}\right)$$
(2)

 $e_{ab}$  and  $S_{ab}$  provide the energy and length scale for the pair interaction, respectively. The bump term b(r) can be written as,

$$b(r) = \varepsilon^{b}_{\alpha\beta}\varepsilon_{AB} \cdot \sin^{2}\left(\pi \frac{r^{c}_{\alpha\beta} - r}{r^{c}_{\alpha\beta} - r^{s}_{\alpha\beta}}\right)$$
(3)

 $\mathcal{C}^{b}_{ab}$  is the height of the repulsive bump term. Note that the bump term itself and its first derivative are zero at both  $r^{s}_{ab}$  (starting distance for the energy penalty) and  $r^{c}_{\alpha\beta}$  (ending distance for the energy penalty). The overall mLJ potential is therefore still smooth after the inclusion of b(r) between  $r^{s}_{ab}$  and  $r^{c}_{ab}$ .

The energy and length units are set up as  $\varepsilon$  and  $\sigma$ , respectively. All particles have the same mass  $m_0$ . The temperature unit is  $\varepsilon / k_B$  ( $k_B$  is the Boltzmann constant), and the time unit is  $t_0 = \sigma \sqrt{\frac{m_0}{\varepsilon}}$ . Table 1 lists the primary parameters for interactions among all nine types of particles. The interaction strength, bond length, and cutoffs are species-dependent and well defined to realize chain-growth polymerization. Note that the bump term is applied to the A-P<sub>A</sub> and B-P<sub>B</sub> interactions, aiming to avoid bond-breaking purely due to thermal fluctuation, and thus retaining the AP and BP particles in the dormant state until the initiator activates them. In addition, there is a bump term for A-B, A-T<sub>A</sub>, B-T<sub>B</sub> such that polymerization and termination reactions require thermal activation. We use LAMMPS <sup>2</sup> as the platform for all the simulations. Newton's equations of motion are numerically integrated using the velocity-Verlet algorithm with a time step of 0.005  $t_0$ . The temperature and pressure are well controlled *via* Nose-Hoover <sup>3,4</sup> thermostat and barostat, respectively. The visualization software OVITO <sup>5</sup> is used to generate simulation snapshots and animations.

#### S.III.II Coarse-grained simulation methodology

The coarse-grained simulation starts with a random mixture of model chemicals of reactants and terminators. The simulation box is 175.5  $\sigma$  by 175.5  $\sigma$  by 117.0  $\sigma$  in size. There are ~110000 A-PA molecules (reactants), ~110000 B-PB molecules (reactants), ~28000 T<sub>A</sub>-E<sub>A</sub> molecules (terminators), ~28000 T<sub>B</sub>-E<sub>B</sub> molecules (terminators) in the system. The total number of particles in the system is around half a million. The system is periodic in both the x- and y-direction. The system has a non-periodic boundary condition in the z-direction. All particles are constrained by two repulsive walls interacting according to the Lennard-Jones 9-3 potential with parameters of 0.0001  $\varepsilon$ , 1.0  $\sigma$ , and a cutoff of 2.5  $\sigma$ . In addition, A- and B-particles are interacting with the bottom wall with additional attraction (0.2  $\varepsilon$ , 1.0  $\sigma$  and a cutoff of 2.5  $\sigma$ ) to mimic the affinity to the silicon substrate. The system is subjected to an isothermal relaxation at a temperature of 0.04  $\varepsilon/k_B$ .

Photon-initiated polymerization is conducted by introducing initiator I molecule via a grand-canonical Monte-Carlo (GCMC) operation into a cylindrical region of the system uniformly. The temperature of the system is held at 0.04  $\varepsilon / k_B$  during the entire polymerization process.

Pair Bond Type	$\mathcal{E}_{\alpha\beta}/\mathcal{E}$	$\sigma_{_{lphaeta}}/\sigma$	$\left. \mathcal{E}^{b}_{lphaeta} \right  \mathcal{E}$	$r^{s}_{lphaeta}/\sigma$	$r^{c}_{lphaeta}/\sigma$
А-А, В-В	0.50	2.0936	0.00	1.00	2.90
А-В	2.20	1.00	0.10	1.00	2.50
A-P <sub>A</sub> , B-P <sub>B</sub>	1.00	0.3564	0.12	1.20	0.57
A-P <sub>B</sub> , B-P <sub>A</sub>	0.05	2.0045	0.0	1.0	2.25
A-I	2.00	1.39	0.00	1.00	1.56
B-I	5.00	1.25	0.20	1.20	2.00
P <sub>B</sub> -I, P <sub>B</sub> -I	0.01	0.3564	0.00	1.00	0.40
A-T <sub>A</sub> , B-T <sub>B</sub>	1.20	1.00	0.22	1.00	2.35
T <sub>A</sub> -E <sub>A</sub> ,T <sub>B</sub> -E <sub>B</sub>	5.00	0.3564	0.25	1.20	1.50
A-E <sub>A</sub> , B-E <sub>B</sub>	0.002	1.8709	0.00	1.00	2.1
A-T <sub>B</sub> , B-T <sub>A</sub> , T <sub>A</sub> -T <sub>A</sub> , T <sub>B</sub> -T <sub>B</sub>	0.1	2.2272	0.00	1.00	2.5
P <sub>A</sub> -T <sub>A</sub> , P <sub>B</sub> -T <sub>B</sub> , I-I	0.02	2.2272	0.00	1.00	2.5
All Other Bonds	0.02	2.85	0.00	1.00	2.90

 Table S1. Species-dependent parameters of the mLJ force field for chain-growth polymerization.



#### S.IV Cluster and reaction progress analysis on the polymeric systems

**Fig. S3.** (a)The size of the largest cluster of the polymeric sample as a function of time. The jumps indicate crosslinking of multiple clusters. The three simulations represent different simulated laser intensity (red is the lowest, blue is the highest) (b) Reaction progress characterized by the unreacted monomers.



#### S.V Simulated and experimental mechanical properties of photo-cured PEGDA samples

**Fig. S4.** (a) Simulated stress-strain curves for polymeric pillars with exposure time of 15, 25,  $35 \times 10^3$  t<sub>0</sub>, for three level of laser intensity (increasing from red, green to blue). (b) Experimental elastic modulus, measured via AFM for different exposure times and laser intensities.

### S.VI Raman spectra of cured PEGDA samples



**Fig. S5.** Raman spectra of PEGDA samples cured at: (a) I=20 for (0.5,1, and 2s) and (b) at I=30 for (0.5,1, and 2s) with reference to pure PEGDA liquid.

# S.VII Raman mapping of cured PEGDA samples



**Fig. S6.** (a) Transverse (x-y) cross-sectional Raman map for the C=O bonds. (b) XZ cross-section of Raman map for C=C bonds indicating a gradient in the un-reacted resin. The schematic describes the sample orientation upon Raman scanning, indicating the curing direction of the sample and the Raman laser. (c)The Raman single intensity variation with position, scanning over the line illustrated in (b).

## References

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