Toward photopolymer resin design for additive manufacturing

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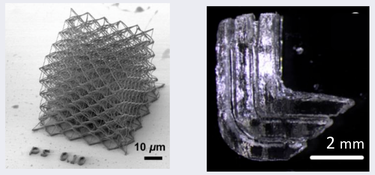
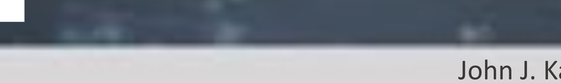
Two-photon polymerization (2PP) techniques continue to increase the resolution of additive manufacturing (AM, a.k.a. 3-D printing) and emerging reverse tomographic approaches discard the 'rastering print head' paradigm. The resolution and print quality of both approaches are limited by the chemistry and physics of the polymeric resin itself. Our recent work uses atomistic monomer models and combinations of classical and reactive molecular dynamics to bridge the gap between atomistic, particle-based models and existing continuum models.



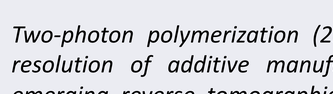
A 2PP-printed free-standing octet-truss cube[1] (left) and LLNL logo (right) fabricated by holographic patterning.[2]

SYSTEMS & METHODS

In the present work we study three acrylate monomers that are commonly used as AM photosensitive resins. Simulation boxes for each of these three systems contain 2000 monomers that were equilibrated in the NPT ensemble at 300 K using the OPLS-UA force field.

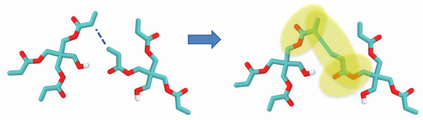


HDDA (left) and PEGDA-250 (right) are bifunctional acrylates of similar size with slightly different functionalities between the acrylate groups.



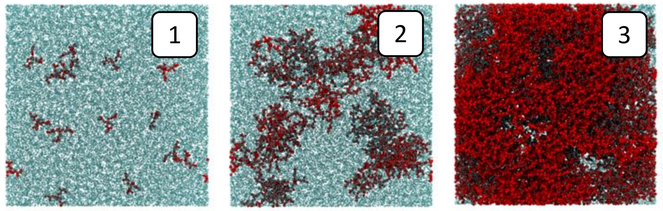
The trifunctional PETA monomer (left) has a higher density of reaction sites. Its corresponding united-atom representation is shown on the right.

To create the polymer network, 20 random vinyl groups (1% of the monomer molecules) are mutated into radical sites at t = 0 to simulate photoinitiation. We use fix bond/react, a proximity-based reaction scheme recently developed by Gissinger et. al.[3] to model diffusion-limited polymerization.



When a radical-bearing PETA monomer 'reacts' with another free PETA monomer the local bond, angle, and dihedral topologies are updated to reflect the new chemical environment.

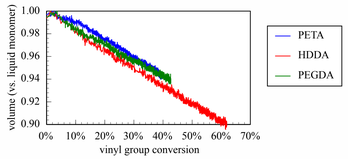
SIMULATED POLYMERIZATION



Molecules with active radical sites (red) rapidly convert the liquid PETA monomer (cyan, transparent). Cubic simulation boxes are approximately 10 nm per edge.

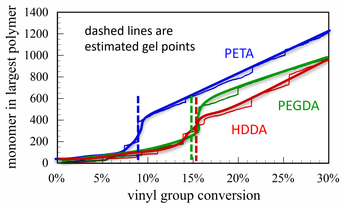
After equilibrating the monomer liquid, the radical sites are allowed to react with nearby free monomer. At the end of the simulation, nearly all of the 20 radicals are present within the final polymer molecule as trapped radicals: active, but not within range of an unreacted vinyl group.

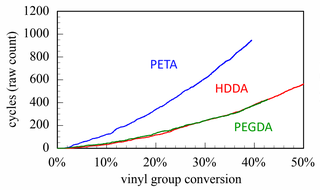
DYNAMIC POLYMER TOPOLOGY

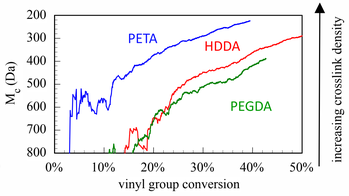


Shrinkage may be quantified on-the-fly during the simulation as the reaction progresses and covalent bonds replace van der Waals forces.

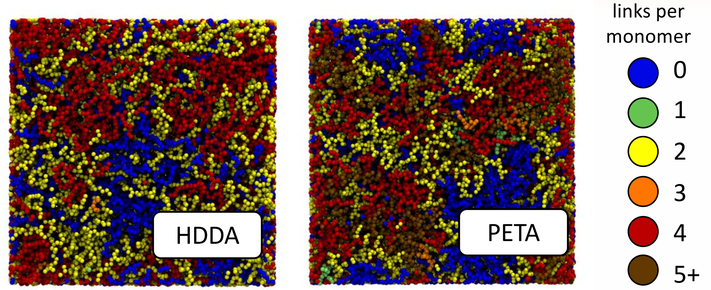
By monitoring the size of the largest propagating polymer, the inflection point is assigned to be the gel point, indicating when the largest percolating mass spans the simulation box.







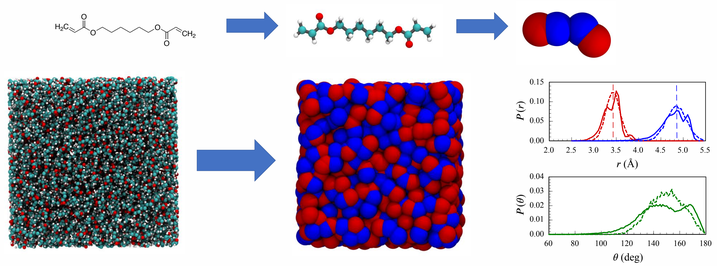
Mathematical graph theory quantifies the loop/cycle and crosslinking densities of propagating polymer networks. These microscopic topological features correlate with macroscopic observables and will be used in future monomer design.



A crosslinking 'heat map' provides molecular insight to polymer chemists. Differences between bi- and trifunctional acrylates are evident in initial simulations.

COARSE GRAINING

Since our interest lies in larger length and time scales, validation of OPLS-based models will be followed by a coarse graining (CG) approach. The same reactive scheme will allow us to explore both MARTINI and Boltzmann Inversion approaches.



Initial MARTINI-based coarse-graining of HDDA reduces the number of particles by a factor of 8.5 and increases the time step by an order of magnitude.

FUTURE WORK

- Expand reactive templates to include other chemical systems of interest.
- Measure physical parameters for model verification and calibration.
- Adapt graph theory-based metrics to analysis of polymer networks.

REFERENCES

1. Oakdale , J. S.; Ye, J.; Smith, W. L.; Biener, J. *Optics Express* **2016**, *24*, 27077-27086.
2. Shusteff, M. *et. al. Science Advances* **2017**, *3*, eaao5496.
3. Gissinger, J. R.; Jensen, B. D.; Wise, K. E. *Polymer* **2017**, *128*, 211–217.

LAMMPS NetworkX

Our goal: Designer photopolymer resins for additive manufacturing informed by molecular mechanics and graph theory.

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