Thermoplasmonic-Induced Phase Separation of Polymer Blends for Multicomponent Photopatterning

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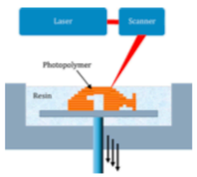
Abstract

Precise spatial control of multicomponent polymer systems is critical for advanced soft materials manufacturing. A method for localized phase separation in thermoresponsive polymer blends using photoinduced electron/energy transfer reversible addition-fragmentation chain transfer (PET-RAFT)-synthesized polymers and gold nanorods (AuNR4) for photothermal heating under near-infrared light (NIR). Optical excitation induces temperature-driven phase separation, enabling microscale patterning without bulk heating. Characterization reveals tunable cloud points, mechanical properties, and rapid heating profiles sufficient to exceed lower critical solution temperature (LCST) thresholds. This thermoplasmonic approach enables scalable, light-directed structuring of polymer domains, offering applications in responsive coatings, additive manufacturing, and functional biomaterials.

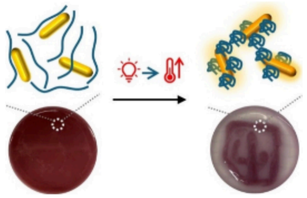
Background

3D Printing Polymers in Resin Solutions



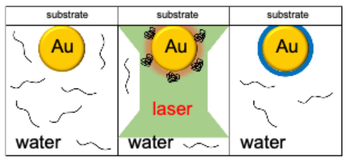
Mater. Res. **2015**, *18*, 1205-1212.

Self-Assembly Driven Microlithography



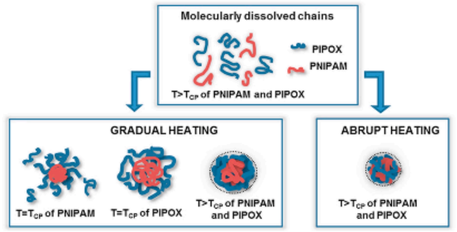
ACS Appl. Polym. Mater. **2026**, https://doi.org/10.1021/acsapm.5c04693

Thermoplasmonic Heat Induced Phase Separation



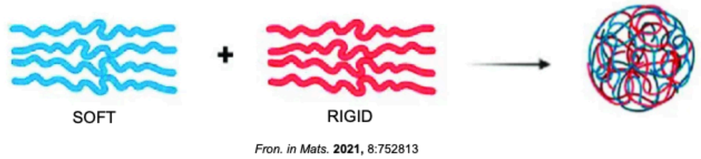
J. Phys. Chem. C **2016**, *120*, 17745-17752.

Temperature Induced Aggregation of PNIPAM in Copolymers



Polymer **2015**, *68*, 65-73.

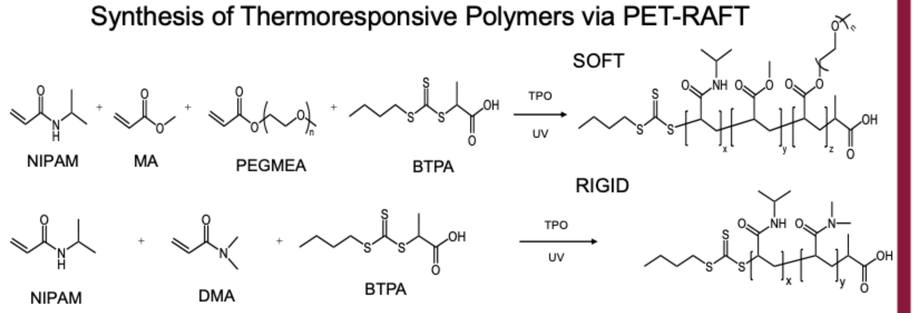
Combined Mechanical Properties from Random Polymerization



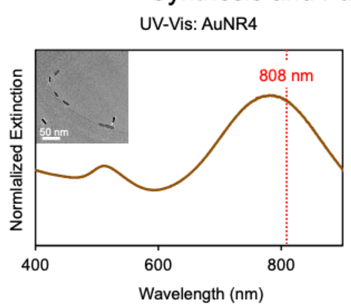
Fron. in Mats. **2021**, 8:752813

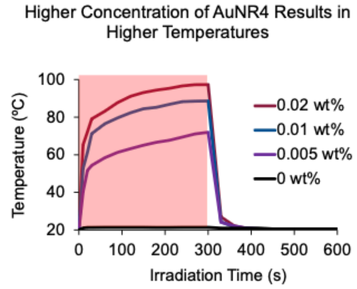
Methods

Synthesis of Thermoresponsive Polymers via PET-RAFT

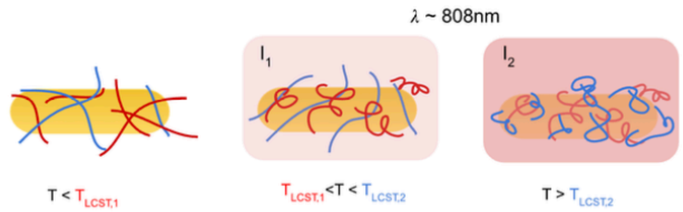


Synthesis and Functionalization of AuNR4



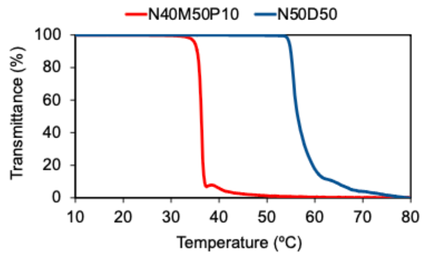


Stages of Microlithography Photopatterning

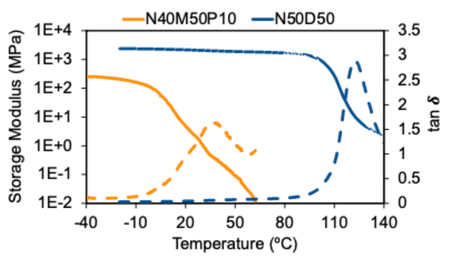


Results / Discussions

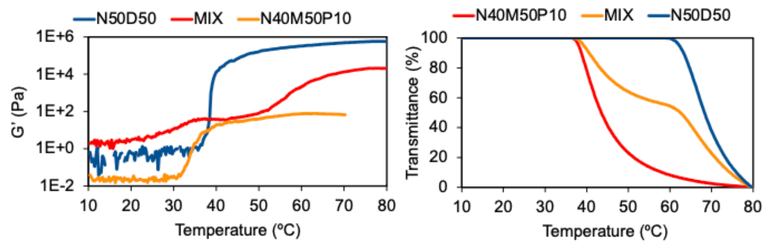
Transition Temperatures of Soft and Rigid Copolymers



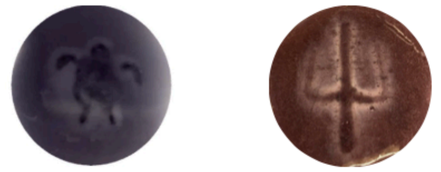
Stiffness of Rigid and Soft Copolymers



Two Transitions are Observed in the Polymer Mixtures



Phase Separated Structures via Laser Printing



Conclusions

An approach for additive manufacturing via phase separation in two different copolymers was achieved. Two blends of random copolymers, both containing thermoresponsive monomer NIPAM, gives a wide variety of mechanical and chemical properties. Tuning the LCST from different compositions allows for different gel properties. Thermochemical properties have minimal variations from the original copolymers versus from in the blend. The printed blends have shifted glass transition temperatures (T_g) based on the original copolymers.

Future Work

Further testing of the printed structures, such as tensile testing and self-healing, will be performed. Scaling the procedure for larger batches and compositional analysis will be done. Testing with ultra-high molecular weights (UHMW) for relaxation kinetics below the LCST will be tested and researched on for re-dissolvable structures.

Acknowledgments

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