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Stimulating Self-Directed Polymer Phase Evolution with Nonlinear Light Waves during Free-Radical Polymerization

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Overview. One of the central aims of the proposed work was to demonstrate the ability to control the evolution of binary phase morphology of photoreactive polymer blends using nonlinear optical waves. Nonlinear optical waveforms propagate divergence-free through a nonlinear optical medium, one characterized by an intensity dependent refractive index. The rise in refractive index owing to polymerization provides a suitable nonlinearity so as to sustain nonlinear optical wave propagation. In turn, the increase in molecular weight of the polymers in the regions of illumination by these waves induces polymerization induced phase separation (PIPS), whereby one polymer blend component occupies the regions of the optical waves, and the other component occupies the dark regions. This is a fundamentally different way to direct the evolution of binary phase morphology, in contrast to uniform illumination and 3D holographic fields.

Research Achievements. With the support of the ACS PRF grant during the 1st year of the award, extensive progress has been made in demonstrating this new nonlinear chemical dynamic phenomenon.

1. In-Situ Studies. The process of binary phase evolution of morphology under irradiation of a periodic array of optical beams was tracked *in situ* using confocal Raman spectroscopy.[1] Evidence of the formation of nonlinear waves as well as the resultant reaction kinetics and phase separation was attained. This research provided conclusive evidence that nonlinear optical waves couples to photopolymerization-induced phase separation, whereby the polymer binary phase morphology is spatially congruent to the arrangement of the array of nonlinear waves (Figure 1).

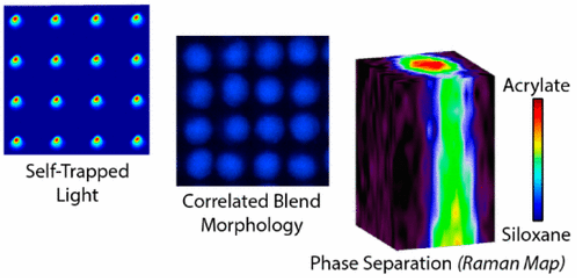

Figure 1. Attainment of congruent patterns between arrays of nonlinear waves and binary phase morphology.

2. Correlating Polymer Blend and Optical Parameters to Morphology. In a series of additional studies, the effect of the irradiation conditions (intensity, beam size and spacing) as well as the polymer blend parameters (weight fraction, χ parameter, and initial molecular weight) on the resultant morphology was investigated.[2] Clear, deterministic and generalized principles were revealed whereby any polymer blend mixture could be directed to organize with a binary phase morphology that is congruent to the array of nonlinear waves. This knowledge was used to create binary phase morphologies over a diverse range of polymer systems and broad range of structures. The principles were also elucidated and confirmed in first of its kind simulations of polymer phase evolution during nonlinear light wave propagation.[3]

3. Demonstration in Photopolymer-Solvent Mixtures. As an expansion and generalization of the principles developed for binary polymer blends, the process of coupling nonlinear waves to phase separation was further demonstrated in photopolymer-solvent mixtures,[4] with the long-term aim to create microporous membrane structures for oil-water separation (Figure 2). In situ studies of the nonlinear wave propagation in photopolymer-mixtures were carried out. It was observed that phase separated structures of the photopolymer (upon solvent removal) are also congruent to the pattern of nonlinear waves, and that the solvent removal leaves remaining a periodically arranged array of micropores. In additional, the presence of nanopores was also observed, resulting in a hierarchical porous structure. The evolution of the phase separation was correlated to the intensity, size, and spacing of the nonlinear optical waves.

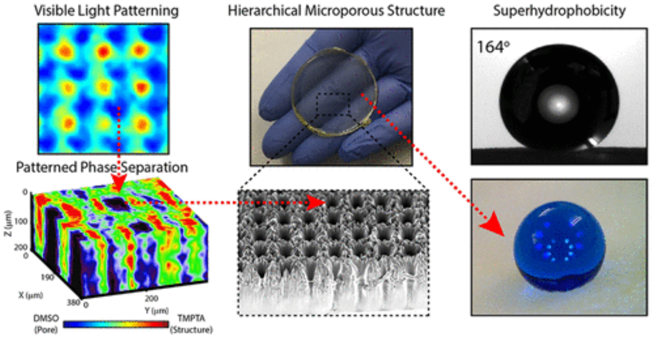

Figure 2. Coupling of nonlinear wave formation to the phase separation of a photopolymer-solvent mixture. Resultant materials have anti-wetting properties, which may be exploited for oil-water separation in the future.

4. Future Work. Future work[5] seeks to explore the process in a broader range of polymer systems, as well as in advanced mixtures such as ternary blends and photopolymer-nanoparticle mixtures. Future work will also focus on further investigating of the organization mechanism in order to, for example, attain membranes with pores that permeated the entire material, towards creating materials for oil-water separation.

Impact on PI's career. Demonstration and deep insight and understanding into the process was one of the key aims and intended contributions of the PI in his tenure track. This support work has established both the PI and his research group is one of the leaders is new and exotic forms of nonlinear chemical dynamics, whereby new material structures and arrangements can be attained. The work has resulted in several high impact journal publications and 2 invited conference lectures, further broadening the reach and impact of the PIs work to the research community. The work now opens opportunities for further investigations of the phenomenon towards creating generalized principles towards directing the phase evolution in a broader range of binary blends, ternary blends, and other composite blends such as polymer-nanoparticle. Hence, the impact has been in establishing a truly unique research program on the basis of this new nonlinear chemical dynamic phenomenon. In addition, the inherent optical properties of the materials has allowed the PI to explore other avenues of research such as membranes for oil-water separations for oil-spill cleanup as well as coatings for solar cells to increase light capture of conversion.[2] To this end, an internal University grant was awarded, and other external funding opportunities have been applied to. Hence, this grant has provided support whereby the PI's career and his lab has reached "critical mass" towards making consistent, stable, and supported contributions to the research community in the area of fundamental and applied polymer science. This supported work has also enabled more complex soft matter systems to be explored in future work, as discussed above.

Impact on Students. This PRF grant has supported the doctoral work of 1 graduate student, and as well as a summer research experience for 1 undergraduate student. The graduate student has been the 1st author on all publications of work supported by this grant, and the work has formed the successful basis of his doctoral thesis that will be defended in 2019. The work has provided him with the necessary skills and knowledge to pursue employment in industry in the area of polymer materials synthesis and characterization. The work of the undergraduate will soon be published with him as first author, and the student has since graduated and sought work in the polymer industry.

References

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