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Stimulating Self-Directed Polymer Phase Evolution with Nonlinear Light Waves during Free-Radical Polymerization
Ian D. Hosein, Syracuse University

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. 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 the illuminated regions become occupied by one polymer component, and the other component is expelled into the surrounding 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 2nd year of the award, extensive progress has been made in correlating the polymer blend parameters as well as the size/spacing of the nonlinear waves to the resulting binary phase morphology.

1. Structure Formation Studies. Leveraging the principles of structure formation and their dependency on irradiation intensity and blend parameters, we now achieved structure-tunable binary phase morphologies (Figure 1).[1] The structures were formed by propagating arrays of optical beams through the polymer blend, which were generated using masks with varying aperture diameters and spacing. This varies the size and spacing of the nonlinear waves that will naturally form in the medium, which will then direct the binary phase morphology to have the same structure. Structures of varied sized and spacing of "filament phases" were produced. This achievement moves the work towards the capability to tune structure towards applications in which polymer blends play critical roles.

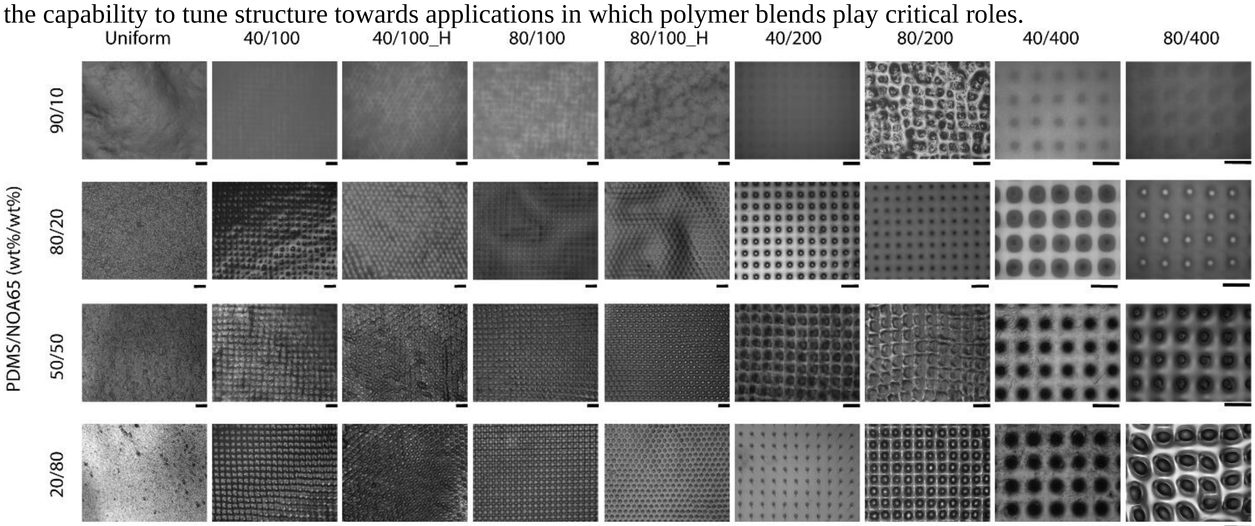

Figure 1. A full range of binary phase morphologies produced by arrays of nonlinear waves of rationally varied size and spacing using blends of different relative weight fractions. Size (D) and spacing (S) of the waves are defined by the D/S ratio. All structures are of square symmetry, except for hexagonal structures indicated by "_H". Scale bars = 100 µm.

2. Polymer-Nanoparticle Morphologies with In Situ Photochemical Reduction of Silver Salts. Advancing the work on structure-tunable binary phase morphologies, we employed polymer blends which also included a silver salt precursor.[2] Concurrently with the polymerization of the blends, as well as phase separation, silver nanoparticles begin to form in the filament phases (polymer cores, component 1) which are uniformly dispersed along the depth of the blends in the regions of illumination (Figure 2). This is an exemplary three component system, and opens opportunities for creating hybrid organic-inorganic multicomponent systems with tailored, organized morphology for a host of applications, including catalysis, anti-wetting, and anti-microbial materials. The silver content was tuned by varying the concentration of silver salt precursor.

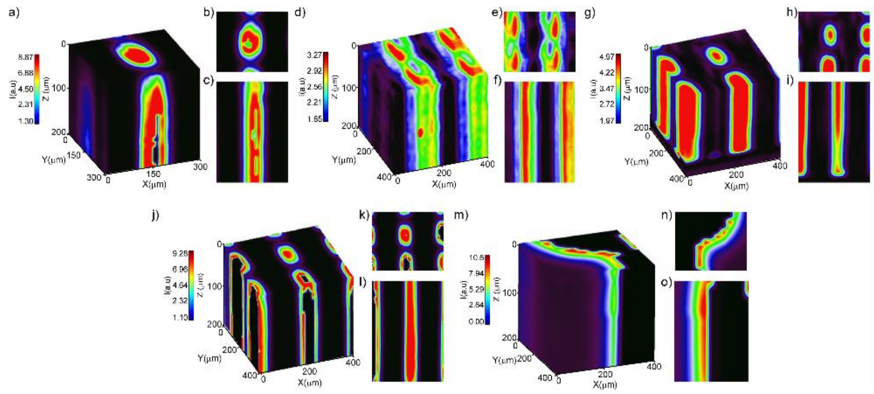

Figure 2. Raman volume map of self-written waveguides with (a, d, g, j, m) 0.1%, 0.5%, 1.0%, 2.0%, and 3% of AgSbF6, respectively. (b, e, h, k, n) xy-slices through the middle the waveguides, revealing their cross-sectional profiles. (c, f, i, l, o) yz-slice through the core central axis, revealing their longitudinal profiles that extend over the depth of the film. Red zones indicate regions in the sample comprising the silver nanoparticles. Black color in the center of the waveguides is an artifact of signal saturation.

3. Future Work. Future work[3] seeks to explore the process in a broader range of polymer systems, which will commence hereon by examining ternary blends, as well as continue to work to synthesize membranes. Similar in situ studies on the kinetics of formation will be pursued, as well as characterization of the resultant structures.

Impact on PI's career. The capability to produce rationally varied binary phase morphologies has been the hallmark of this year's work, and one of the final milestones of the research, namely showing that nonlinear waves can enable structure-tunable morphologies. This has further pushed both the PI and his group to be leaders in the area of control of polymer blends. As a result of this impact, the PI's work has been featured on two journal covers, 2 conference invitations, thereby further broadening the impact. The work has also enable the PI to acquire funds from NSF through a standard grant to continue a branch-off direction of the work for thin-film optics.

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 2020. 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. In fact, the doctoral student has received a 6-month internship to work for the polymer company Sartomer, as a result of his research achievements and skills.

References

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2. Biria, S.; Wilhelm, T. S.; Mohseni, P. K.; Hosein, I. D., Direct Light-Writing of Nanoparticle-Based Metallo-Dielectric Optical Waveguide Arrays Over Silicon Solar Cells for Wide-Angle Light Collecting Modules. *Adv. Opt. Mater.* **2019,** *0*, 1900661.
3. Biria, S.; Morim, D. R.; An Tsao, F.; Saravanamuttu, K.; Hosein, I. D., Coupling nonlinear optical waves to photoreactive and phase-separating soft matter: Current status and perspectives. *Chaos: An Interdisciplinary Journal of Nonlinear Science* **2017,** *27*, 104611.