

A Narrative Statement Report in 2011: ACS-PRF grant # 48735-ND7

*Research and Education Activities:*

Prior to investigating the *trans-cis* photoisomerization effects, we found gigantic azobenzene pyramid single crystals shooting through monomer and nematic liquid crystal melt phases. The shooting phenomena is present in trimethylolpropane triacrylate (TMPTA), 1,6-hexanediol diacrylate (DA), and E7 nematic liquid crystals. We established the solid-liquid phase diagram of AC and each of the solvating components above, showing isotropic, pure crystalline, and coexistence of crystal + isotropic regions bound by solidus and liquidus lines. Upon thermal quenching from the isotropic melt to the crystal + liquid region, AC crystals nucleate and form faceted rhomboidal single crystals. As solvent is rejected from a growing front, a concentration depletion zone develops at the crystal-solution interface. This composition gradient induces spatial variability of surface tension, a relation known as the Marangoni effect. If single crystals nucleate in this surface tension gradient, they are propelled away from the growing front by unequal surface tension forces. Such crystal rapid motion (hereafter called crystal shooting) has prompted development of a model for the motion based on the balance between surface tension and opposing drag forces. The mathematical model has resulted in one publication and another one in progress in collaboration with Professor Dmitry Golovaty from the Department of Applied Mathematics.

Crystals which move quickly through the solution also appear to take on shape selection rules based on solution undercooling. A fourfold rhomboidal symmetry is exhibited at shallow undercoolings, while the rhomboidal shape becomes truncated at the acute tips, creating a six-fold crystal symmetry in crystals observed at deeper solution undercoolings. A phase field model for crystal solidification is being developed to simulate crystal shape selection rules, the phase field model is advantageous in that the thickness of the interface affects the front propagation speed and shape. Also, the surface energy anisotropy of growing single crystals is incorporated into the model so as to preferentially grow the crystal along certain crystallographic planes. We hypothesize the relative growth rates along crystallographic planes changes with undercooling depth, much like the shapes of snowflakes depend on saturation conditions in the clouds they grow in. Once shape selection behavior is characterized in relation to the phase diagrams, we plan to use these guiding principles during photo-patterning experiments to select the preferred crystal interface topologies.

*Students Involved and/or Graduated:*

Namil Kim, graduated with a Ph. D. in August, 2010 with the dissertation supported by this ACS-PRF grant # 48735-ND7: "Photoisomerization and photopolymerization induced phase transitions in mixtures of photoresponsive chromophores and reactive mesogens". Dr. Kim has been working as a research fellow with a Korean national lab. Grant Riley, an undergraduate Physics student from Miami University (OH) studied AC crystal motion in diacrylate during summer 2010 (10 weeks) and was jointly supported by NSF-REU. Tom Sutter, a Ph. D. candidate, is currently exploring the AC/E7 liquid crystal system, modeling the crystal solidification, and developing a photolithography setup to complete the second focused area of the grant. He presented crystal motion findings at the 2011 APS national meeting in Dallas, TX, and also at the Midwest regional ACS meeting in 2011. Tom Sutter won the University of Akron poster contest for graduate research in May 2011. Kaitlin Sweany, an undergraduate Physics student from Baldwin Wallace College studied shape selection of AC crystals in E7 blends during summer 2011 (10 weeks) and was

jointly supported by NSF-REU. Jonathan Proch, an undergraduate student in mathematics and electrical engineering, was hired during summer 2011 for 2 months to perform the numerical simulation on crystal growth dynamics and was supported by the present PRF grant.

*Publications:*

1. K. Milam, G. O'Malley, N. Kim, D. Golovaty, and T. Kyu, "Swimming Photochromic Azobenzene Single Crystals in Triacrylate Solution" *J. Phys. Chem. B*, 114, 7791-7796 (2010).
2. N. Kim, H. Lam, and T. Kyu, "Photochromism and photopolymerization induced mesophase transitions in mixtures of spiropyran and mesogenic diacrylate," *J. Phys. Chem.*, 114, 16381-16387 (2010).
3. N. Kim, Q. Li, and T. Kyu, "Effects of *Trans-Cis* Photoisomerization on Phase Equilibria and Phase Transition of Liquid Crystalline Azobenzene Chromophore and Its Blends with Mesogenic Diacrylate," *Phys. Rev. E*, 83, 031702 (2011).
4. N. Kim, T. Sutter, T. Kyu, and D. Golovaty, "Crystal Nucleation and Motion: A New Type of Growth Instability", *to be submitted* (2012).

*Major Findings:*

- 1) The present research is the first to demonstrate the swimming, shooting, and sinking of diamond AC crystals during crystallization in solution.
- 2) The phenomenon of crystal swimming is attributed to the unbalanced surface forces resulting from solvent rejection from growth fronts and a solvent concentration gradient. This novel surface tension mechanism is the first to be reported in the field of crystal growth.
- 3) AC single crystals in diacrylate solutions are capable of undergoing cascading nucleation events while moving through the melt, resembling fireworks. Tumbling while shooting, and varied single crystal shapes (hexagonal or rhomboidal) are the never before seen phenomena.
- 4) Polygonal shape selection during crystal growth is due to the depth of undercooling below the liquidus line of the system.
- 5) Deep temperature quenches below the liquidus reveal seaweed-type crystals growing in regions of lowest temperatures and polygonal single crystals at temperatures at shallower depths. Complexity of possible crystal structures is conceptualized in the context of the undercooling depth guided by the phase diagram.

*Proposed Study in the Third Year (i.e., no-cost time extension period)*

In the requested no-cost time extension period, we will examine AC crystal solidification and motion during photolithographic illumination and patterned photopolymerization of DA. The spatio-temporal crystal growth will be investigated in the context of phase field theory of solidification by coupling with the photopolymerization rate. The influence of photopolymerized DA domains on crystal motion and shape selection will be explored. We expect the liquidus of AC/DA blends to move to higher temperatures as a result of the photopolymerization, in turn creating more truncation in single crystals or evolution of the solidification fronts into dendritic or seaweed structures.