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**This report describes a cooperative project between Rice University and National Tsing Hua University researchers focused on synthesis and processing, morphology and physical characterization of chiral block copolymer (BCP) materials. Such materials are valuable for both their optical and mechanical properties, particularly for their potential as chiral metamaterials and lightweight energy absorbing materials. The effort examined the cylinder to helical transition (C to H\*) and investigation of self-assembly of chiral block copolymer into the double gyroid (DG\*) block copolymer. With the presence of either a right or left handed chiral block investigations centered on the transfer of the molecular scale chiral information to the microdomain scale in these microdomain geometries as well as measuring the physical properties. A simple method was developed for the preparation of new network nanomaterials by removing the matrix in the double network structure, allowing the respective networks to displace small amounts in arbitrary directions from the initial high symmetry positions in the Ia3d space group to a lower symmetry arrangement resulting in a sub space group, the I4132. Experimentally the original copolymer networks were converted into inorganic networks by using hydrolyzed diblocks as a template for a sol-gel reaction in the empty channels. Thermal annealing of the inorganic network resulted in a single gyroid (SG). The approach developed a platform process technology that can fabricate novel network morphologies from initial bicontinuous cubic phases through supergroup/subgroup transformation.**

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**“Chiral Block Copolymer Structures for Metamaterial Applications”**

**January 27, 2015**

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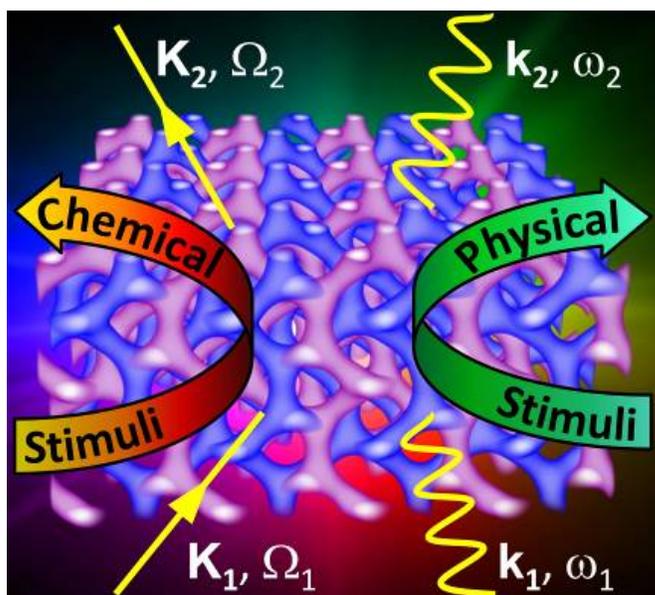
**Abstract:**

This cooperative program between Rice University and National Tsing Hua University researchers focused on the synthesis and processing, morphology and physical characterization of chiral BCP materials. Such materials are valuable for both their optical and mechanical properties, particularly for their potential as chiral metamaterials and lightweight energy absorbing materials. We choose to concentrate our work on the cylinder to helical transition (C to H\*) and to investigate the self assembly of a chiral block copolymer into the double gyroid (DG\*) block copolymer. The DG\* structure is a microdomain geometry with body cubic symmetry and space group Ia3d. It is normally comprised of two interpenetrating and opposite handed chiral networks, related by inversion symmetry forming a bicontinuous microstructure. With the presence of either a right or left handed chiral block, we were interested in the transfer of the molecular scale chiral information to the microdomain scale in these microdomain geometries as well as measuring the physical properties.

**Introduction:**

Metamaterials<sup>1</sup> have been shown to be able to exhibit extraordinary effective properties, such as negative refractive index, negative dynamic modulus and/or density, phononic band gaps, superior thermoelectric properties, and high specific energy absorption. Structures such as the H\* may act as broadband circular polarizers for optical information processing. Nanoporous inorganic materials with high porosity, high surface area, high crushing strength and low bulk density can be used as high reactive

catalysts and supports for mediating various organic transformation reactions. Such metamaterials depend on precise nanofabrication of complex topological and geometrical structures. Nanostructured networks are a very fascinating morphology due to their lightweight, high porosity and large specific surface areas as well as superior mechanical properties with self-supporting character. Although many technologies have been explored to fabricate nanostructured networks, templated synthesis is one of the most important approaches to fabricate nanostructured materials with precisely controlled structures and morphologies from constituted components. The idea is to use the organic block copolymer to form the structure and then by suitable selective etching and back filling – ceramic, metallic etc nanocomposites at the length scale of the original block copolymer structure can be produced. Self assembly of block copolymers (BCPs) is a highly promising route to such structures with length scales in the 10-50nm range, thus affording pathways to interesting new optical and mechanical properties.



**Figure 1** shows a cartoon schematic of the blue/red networks in the double gyroid structure. Conceptually, the ability to stimulate with either chemical or physical means allows one to detect changes in mechanical waves or electro-magnetic waves incident upon the structure.

### Results and Discussion:

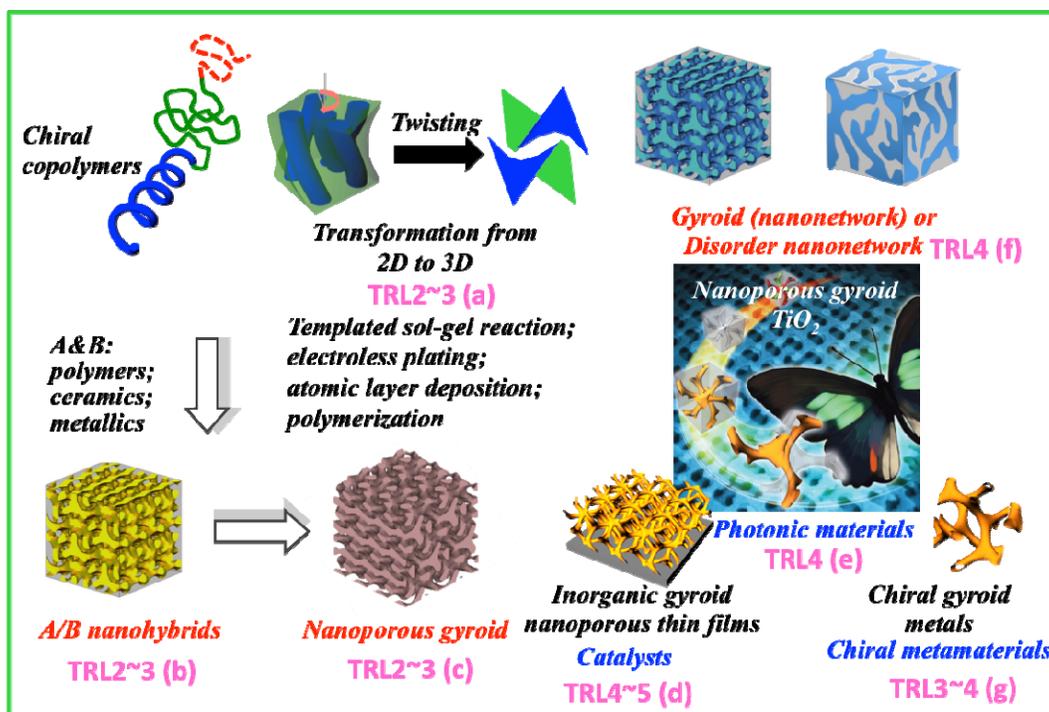
Our partner, the Ho group (Taiwan) synthesized various BCPs which form self assembled geometries including the desired chiral H\* phase and the double gyroid DG\* morphologies. The polymer components are polystyrene and poly l-lactic acid (PS-PLLA) connected together by a covalent bond to form diblocks. The synthesized BCP samples have different molecular weights and compositions, leading to different structures, periodicities and feature sizes. Note that the PLLA block is easily degraded and removed by an aqueous base. The ability to remove the PLLA component, creates

nanocomposites comprised of hollow air cylinders in a PS matrix or an air matrix surrounding two PS gyroid networks. These structures have very high mechanical impedance contrast to the giant difference in modulus of the PS vs. air as well as significant dielectric contrast between the PS domains and the air. The Thomas group performed optical and nanomechanical measurements on the corresponding PS/air nanoporous composites.

The first goal of this project was to carry out the synthetic production of poly(lactide)-containing BCPs\*. A combination of addition polymerization (for the generation of the polystyrene block) and ring opening polymerization (for the generation of the poly(lactide) block) was used. In order to simplify the reaction procedure and to improve the production efficiency as well as to reduce the production cost of the BCPs\*, a one-pot synthetic procedure was developed by the Ho group, employing relatively green chemistry procedures. Moreover, by taking advantage of easy processing and flexible characteristics for polymeric materials, thin-film technologies for facile fabrication of nanoporous materials for templating, in particular with network morphologies, as templates could be developed.

BCPs comprising chiral entities were designed to fabricate novel nanostructured phases via self-assembly<sup>2</sup>. A helical phase (H\*) with controlled handedness was discovered in the self-assembly of polystyrene-*b*-poly(L-lactide) (PS-PLLA) BCPs<sup>3</sup>. Detailed high resolution 3D reconstruction of both the H\* and DG\* BCP microdomain structures using TEM - tomography to analyze the helical, cylindrical, and gyroid microdomain nanostructures showed the effective transfer of chiral information from the molecular level to the micro and macrodomain levels. This joint work<sup>3</sup> was published in the Journal of the American Chemical Society and highlighted by the ACS in 2012. Most interestingly, a wide region for DG\* formation in the phase diagram was found, implying that H\* can serve as an intermediate for the formation of the double gyroid (DG) due to an easy path for order-order transition from 2D to 3D (network) structure.<sup>4</sup> The formation of this new phase and the wide compositional region for double gyroid formation is due to the use of a chiral block.

After the nanoporous polymer templates were made from the nanostructures by hydrolysis, nanoindentation was used to examine the nanomechanical properties of these nanoporous materials. Considerable effort was made to create large grain samples so that the anisotropies inherent in the various microdomain geometries could be explored. Evaluation of the optical properties of the polymer, hybrid, and metallic helical structures produced were hindered by the small grain size of the self assembled periodic microdomain structures and the presence of many structural defects. The superposition of the mechanical or optical responses from many small grains did not enable acquisition of the true property signatures of the chiral phases H\* and DG\*.



**Figure 2** shows how chirality at the molecular scale is transmitted to high order domain structures such as the double gyroid network structure in BCP\*s. By use of an etchable block such as PLLA, various nanohybrid structures can be produced via metallization or infiltration by a sol-gel forming material.

We developed a simple method for the preparation of new network nanomaterials by removing the matrix in the double network structure, allowing the respective networks to displace small amounts in arbitrary directions from the initial high symmetry positions in the  $Ia3d$  space group to a lower symmetry arrangement (the two networks become incoherent due to the small random displacements) resulting in a sub space group, the  $I4_132$ . Thus, a double gyroid (DG) structure from the self-assembly of polystyrene-*block*-poly(L-lactide) (PS-PLLA) was used as a model system for the demonstration of displacing the two originally coherent networks related by inversion symmetry to achieve an incoherent structure with subgroup symmetry not having any inversion symmetries. Thus the supergroup ( $Ia3d$ ) symmetry properties (in this case the scattering of low  $q$  vector xrays) was altered to give the subgroup symmetry ( $I4_132$ ) by means of measuring the experimental low  $q$  xray peak intensities of the annealed PS-PLLA DG structure and the etched inorganic networks/air structure. Experimentally the original PLLA networks were converted into inorganic networks by using the hydrolyzed PS-PLLA as a template for a sol-gel reaction in the empty PLLA channels. Owing to the PS polymer matrix, two registered bicontinuous (DG) inorganic networks form initially. These inorganic networks can be made incoherent by high temperature thermal annealing to remove the PS matrix and allow the nanohybrid networks to physically shift with respect to each other in every grain of the overall sample. The resultant material exhibits an xray scattering signature of a single gyroid (SG). Our approach thus developed a platform process technology that can fabricate

novel network morphologies from initial bicontinuous cubic phases through supergroup/subgroup transformation<sup>5</sup>.

We also investigated the chiral properties of these DG\* and in particular H\* materials. We used the transfer matrix method for optical/photonic crystal simulations. Band diagrams for the SG and DG structures were also computed<sup>5</sup>. However, all optical measurements of the H\* type samples were inconclusive due to the small grain size and numerous defects. Future applications might include novel network morphologies for application in UV reflection for UV LED devices to achieve brighter devices and better energy-saving devices. Also, incoherent shifted networks in very small grain size materials with only short-range order texture could provide organic *amorphous* photonic crystals (APCs) with a visible-wavelength photonic isotropic (angle - independent) bandgap.

We were invited to write a review<sup>6</sup> for *Advanced Materials* focused on ordered photonic and phononic structures made primarily from polymers. We presented the basic ideas of band structures, design principles, selected fabrication techniques, research trends such as metamaterials as well as promising material systems for experimentally accessing these emerging ideas. The elaboration of *polymeric materials* for PhC/PnC will enable further engineering of photons and phonons in both fundamental and applied aspects by virtue of a number of advantages of polymers including their wide range of mechanical properties, ease of functionalization, ability to template/host other optical and mechanical additives and fabrication without costly equipment. In particular, polymeric based PhC/PnC structures are readily *dynamically reconfigurable*, both as switchable geometrical structures and as tunable materials that can respond to a very wide range of physical and chemical stimuli. Chiral geometrical structures containing chiral molecular entities promise to provide many future promising directions for both fundamental research and technological applications.

## References:

1. Lee, J-H., Singer, J.P., Thomas, E.L., "Micro-/Nano-Structured Mechanical Metamaterials," *Advanced Materials*, 24, 4782 – 4810 (2012)
2. Ho, R.-M., Chiang, Y.W., Lin, S.C., Chen, C.K., "Helical Architectures from Self Assembly of Chiral Polymers and Block Copolymers," *Progress in Polymer Science* 36, 376 (2011).
3. Ho, Rong-Ming, Li, Ming-Chia, Lin, Shih-Chieh, Wang, Hsiao-Fang, Lee, Yu-Der, Hasegawa, Hirokazu, Thomas, Edwin L., "Transfer of Chirality from Molecule to Phase in Self-Assembled Chiral Block Copolymers," *Journal of the American Chemical Society*, 134 (26), 10974 – 10986, (2012).
4. Wang, H.F., Yu, Y. H., Wang, X.B., Ho, R.-M., "A Facile Method to Fabricate Double Gyroid as a Polymer Template for Nanohybrids," *Macromolecules* 47, 7993, (2014).

5. H.-Y. Hsueh, Y.-C. Ling, H.-F. Wang, L.-Y. Chan Chien, Y.-C. Hung, R.-M. Ho and E. L. Thomas, "Shifting Networks to Achieve Subgroup Symmetry Properties', *Advanced Materials* 26, 3225-3229 (2014).
6. Lee, J-H., Koh, C. Y., Singer, J. P., Jeon, S-J., Maldovan, M. and Thomas, E. L., "Ordered Polymer Structures for Engineering of Photons and Phonons, *Advanced Materials*, 26 (532-569 (2014).

**List of Publications and Significant Collaborations that resulted from your AOARD**

**supported project:** In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:  
papers published in peer-reviewed journals

1. Lee, J-H., Singer, J.P., Thomas, E.L., "Micro-/Nano-Structured Mechanical Metamaterials," *Advanced Materials*, 24, 4782 – 4810 (2012)
2. Ho, R.-M., Chiang, Y.W., Lin, S.C., Chen, C.K., "Helical Architectures from Self Assembly of Chiral Polymers and Block Copolymers," *Progress in Polymer Science* 36, 376 (2011).
3. Ho, Rong-Ming, Li, Ming-Chia, Lin, Shih-Chieh, Wang, Hsiao-Fang, Lee, Yu-Der, Hasegawa, Hirokazu, Thomas, Edwin L., "Transfer of Chirality from Molecule to Phase in Self-Assembled Chiral Block Copolymers," *Journal of the American Chemical Society*, 134 (26), 10974 – 10986, (2012).
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papers published in peer-reviewed conference proceedings

N/A

papers published in non-peer-reviewed journals and conference proceedings

N/A

conference presentations without papers

Thomas, E.L., "Directed Assembly of Block Polymers," *Bulletin of American Physical Society* 60 (2014)

Thomas, E.L., "Periodic Bicontinuous Polymer Nanostructures," *Abstracts of Papers of the ACS* 245 (2013)

Thomas, E.L., "Periodic Polymers," *APS Meeting Abstracts* 1, 11005 (2013)

Thomas, E.L., "Award Address (ACS Award in Polymer Chemistry, sponsored by ExxonMobil, Abstracts of Papers of the ACS 243 (2012)

provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

We have been in continuous contact with Dr. A. Urbas of WPAFB concerning our works on chiral photonic structures. Dr. Urbas is interested in metamaterials for optical applications in optical limiting (sensor protection).

**Attachments:** Publications a), b) and c) listed above if possible.

Pdfs: attached to email (multiple emails)

**DD882:** As a separate document, please complete and sign the inventions disclosure form.

See accompanying pdf.