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Chirality Transfer to Mesoscale Network Assemblies

Gregory Grason MASSACHUSETTS UNIV AMHERST MA 70 BUTTERFIELD TERRACE AMHERST, MA 01003-9242

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14. ABSTRACT Motivated by ongoing experimental stucopolymers possessing an intrinsically check the chiral organization of chain segmen the relationship between mesochiral ge domains, within two distinct types of me determine how they exhibit variable deg morphologies in chiral triblocks. Addition applied to quantify the mesoscale hand first time. Third, two classes diblock cope morphology, were compared related to of complex, Frank Kasper (FK) phases in framework to investigate the diblock for resolved a previously outstanding puzzle lattice) in the regime where outer block.	udies by IAt iral block, ts within se ometry of t sochiral ge grees of int ally, a rece dedness of blymers with the predic model i e regarding s of sphere	NTP collaborator, Ron an orientational self-c f-assembled periodic he domain shapes ar ometries. First, non-cu ra-domain segment t ently developed anal the alternating gyroic to type different types stions of the mean-fie informationally asymm DFM) of optimal sphe the optimal geometr	g-Ming Ho (Natl consistent field (a , triblock nanosi nd the distributic ubic variants of t wist, which sugg ysis of electron t I network phase of chiral chain o Id oSCF framew metric block cop prical domain su y and free ener	Tsing Hua Ur SCF) theory ructures. This on and magr he alternatir lests a new n omography formed by c chemistry, bu ork. Finally, n polymers by f perlattices w gy of the the	niv., Taiwan), on the self-assembly ABC triblock framework was developed and used to study s oSCF theory was applied to understand how nitude of inter-segment twist within chiral ng gyroid morphology were investigated to nechanism to stabilize non-cubic network reconstructions from the Ho group was assemblies chiral triblock copolymers for the that both form the same chiral mesodomain notivated by recent experimental observations Bates and coworkers, a new computational vas developed. Results of this theory have ermodynamically favored state (the sigma
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PI and Co-PI information: Gregory M. Grason; grason@mail.pse.umass.edu; University of Massachusetts; Department of Polymer Science and Engineering; 120 Governors Drive, Amherst, MA, 01003 USA; Phone: +1 413 577-1611; Fax: +1 413 545-0082

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Abstract: Motivated by ongoing experimental studies by IANTP collaborator, Rong-Ming Ho (Nat'l Tsing Hua Univ., Taiwan), on the self-assembly ABC triblock copolymers possessing an intrinsically chiral block, we have developed and applied an orientational self-consistent field (oSCF) theory framework to study of the chiral organization of chain segments within self-assembled periodic, triblock nanostructures. We have applied this oSCF theory to understand how the relationship between "mesochiral geometry" of the domain shapes and the distribution and magnitude of inter-segment twist within chiral domains, within two distinct types of mesochiral geometries. First, we have investigated how non-cubic variants of the alternating gyroid morphology exhibit variable degrees of intra-domain segment twist, which suggests a new mechanism to stabilize non-cubic network morphologies in chiral triblocks. Additionally, we have applied a recently developed analysis of electron tomography reconstructions from the Ho group, to quantify the mesoscale "handedness" of the alternating gyroid network phase formed by assemblies chiral triblock copolymers for the first time. Third, we conducted a comparative study of two classes diblock copolymers with type different types of chiral chain chemistry, but that both form the same chiral mesodomain morphology, and related the comparison to the predictions of the mean-field oSCF framework. Finally, motivated by recent experimental observations of complex, Frank Kasper (FK) phases in melts of conformationally asymmetric block copolymers by Bates and coworkers, we have developed a new computational framework to investigate the "diblock foam" model (DFM) of optimal spherical domain superlattices. Results of this theory have resolved a previously outstanding puzzle regarding the optimal geometry and free energy of the thermodynamically favored state (the sigma lattice) in the regime where outer blocks of sphere forming copolymers are stiffer than core domains.

Introduction: The overarching goal of this joint theory/experiment project is to understand the influence of chirality transfer from the chain backbone to the handedness, symmetry and hierarchical structure of periodic networks formed by chiral triblock terpolymer self-assembly. Achiral ABC terpolymers are known to form alternating double-gyroid (aDG) structures that spontaneously break the chiral symmetry associated distributing A and C end-blocks to two constituent, left- and right-handed single-gyroid (SG) networks. The central issue addressed in this project, and a crucial step towards engineering the photonic or metamaterial properties of chiral block copolymer assemblies, is the ability of a single chiral block to thermodynamically bias the *global handedness* of the aDG phase, to predictably direct the assembly of distinct A and C domains within the respective left- and right-handed SG subnetworks, leading to a chiral alternating network phase that we denote as chiral alternating double gyroid (aDG*).

This project, we have worked closely with experimental collaborator Ho to analyze the emergent chirality at the mesoscale, of self-assembled networks of a new class of ABC triblocks,

polyisoprene-*b*-polystyrene-*b*-polylactic acid (PI-PS-PLA) copolymers possessing stereopure lactic acid blocks (PDLA or PLLA), or achiral (PLA), synthesized and studied in his group. We have developed a computational algorithm to numerically measure the handedness and "degree" of chirality of aDG* from experimentally extracted 3D electron tomography reconstructions of PI domain single-gyroid networks. From this, for the first time, we are able to relate the "handedness" of the network to the stereochemistry of chiral block (PLA) chemistry from which it is formed.

Theoretical aims by Grason have focused on exploring the relationship between mesoscale chirality in self-assembly structures for in chiral triblocks and the underlying patterns of inter-segment twist which drive thermodynamics in these assemblies using a recently developed orientational self-consistent field (oSCF) theory. Major progress in this effort has been on the computational side extending the resolution limits of the oSCF framework to accurately compute the dependence of net segment twist on morphology, and notably, extend these methods up to the segregation strengths relevant to the experimental study. From this, we are computing the phase diagram of chiral triblock networks for comparison to experimental study by Ho.

A second collaborative effort has stemmed from the recent synthesis of a new chiral block copolymer (BCP*) chemistry by Ho. Previous experimental work showing mesochiral domain assembly from BCP* has been exclusive based on a *single chiral polymer block chemistry*, chiral poly(D or L) lactic acid (PDLA or PLLA). A new class of chiral diblocks incorporates chiral polycyclohexylglycolide(PDCG or PLCG), which differs from PLA in terms of bulkier side group added to chiral backbone. Morphological and spectroscopic studies of PCG and PCG-based BCP*s show the formation of the helical cylinder phase, H*, so far only previously observed for PLA-based diblocks. This is important because it is the first experimental evidence that the mechanisms underlying chirality transfer to the H* helical domain shape are not specific to a particular chiral polymer chemistry, and further, it facilitates a comparative study of the PLA- and PCG- based diblocks and their putative placement on the phase diagram predicted by the oSCF theory of chiral diblocks by Grason.

A final theoretical effort carried out during this project to understand the thermodynamics of complex phase domain formation in block copolymers. While "standard" diblock copolymer phase diagrams exhibit an equilibrium phase showing only the body-centered cubic (BCC) phase of spherical domains, recent experimental observations by Bates and coworkers have shown that for "conformationally asymmetric" diblocks (possessing a stiff outer block and a relatively flexible inner block) a host of complex sphere arrangements may be realized, from Frank Kasper structures (A15, sigma, C14 and C15) to dodecagonal quasi-crystalline phases. These observations have reopened the door to understanding the basic models of long-range order formation in block copolymers. We have developed a new approach to understand the appearance and relatively stability of these complex sphere phases in terms of geometric "diblock foam" model. This model captures the essential features of thermodynamics of competing sphere phases in terms of the shape of the "cells" into which distinct spherical domains are partitioned, further, allows us to understand how competing sphere arrangements compare in terms of relative costs of chain stretching and inter-block repulsions. Critically, we have leveraged the oSCF theory of diblocks to related the "foam model" to a molecular scale theory of sphere phases domain shapes based on the first analysis of the orientational order parameter off segments within the spherical domains of BCP.

Theoretical Methods: To analyze the multi-scale structure self-assembled ABC copolymers in periodic network morphologies, we applied a newly developed oSCF framework to their This theory models the thermodynamics of triblock melts using a similar equilibrium structure. coarse-grained description as the canonical SCF approach, based on a free energy = F =where $f_{FH} = \chi_{AB}\phi_A\phi_B + \chi_{AC}\phi_A\phi_C + \chi_{BC}\phi_B\phi_C$ describes Flory-Huggins $\rho_0 \int dV f_{FH} - TS_{chain}$ interactions between unlike components and S_{chain} is the entropy of chains. The mean-field free energy and chain distributions of the self-assembled states can be solved for (via SCF computational algorithms) given inter-block repulsion and lengths of polymer blocks. Our aims focus on the alternating cubic network mesophase morphologies, where the A and C blocks self-organized into disjoint tubular networks surrounded by a matrix of the B chains, and other mesochiral morphologies, such as cylinder domains A in a C matrix decorated by helical mesodomains of B. To the canonical SCF approach, we add a calculation of the *nematic* order parameter of segments in the A block, which we consider to be the chiral end block (PLLA or PDLA), $Q_{ii}(\mathbf{x}) = \rho_0^{-1} \sum_{\alpha \in A} [(\hat{\mathbf{t}}_{\alpha})_i (\hat{\mathbf{t}}_{\alpha})_i - \delta_{ii}/3] \delta(\mathbf{x} - \mathbf{x}_{\alpha})$ as well as a *polar* order parameter $\mathbf{p}(\mathbf{x}) = \rho_0^{-1} \sum_{\alpha \in A} \hat{\mathbf{t}}_{\alpha} \,\delta(\mathbf{x} - \mathbf{x}_{\alpha}).$ Q(x) is well-known in the coarse-grained modeling of liquid crystalline phases of small molecules, although the spatial profiles of nematic order of segments composing block chains within self-assembled domains have only been recently modeled (by our While Q(x) tracks A segment orientation as "headless vector", the polar order group). parameter $\mathbf{p}(\mathbf{x})$ is distinct in that assigns a vector orientation to segments (and their interactions). Previously our group has shown that these distinct order parameters describe geometrically distinct aspects of segment texture within domains: nematic order is dominated by parallel alignment at the inter-domain surface, while polar order parameter shows segment alignment to be normal to that interface deep in the "brush" domain of the microdomain. Here, we adapt a standard approach to the modeling of chiral (cholesteric) phases of liquid crystals to model the free energy of chiral segment packing in self-assembled domains of ABC triblocks. We consider an excess free energy associated with chiral segment packing of the form, $F^*[\mathbf{Q}(\mathbf{x})] =$ $\frac{\rho_0}{2}\int dV \left[K_1(\nabla \cdot \mathbf{Q})^2 + K_2(\nabla \times \mathbf{Q} + 2q_0\mathbf{Q})^2\right] \text{ or } F^*[\mathbf{p}(\mathbf{x})] = \frac{\rho_0}{2}\int dV \{K_1(\nabla \cdot \mathbf{p})^2 + K_2[(\nabla \times \mathbf{p}) + q_0\mathbf{p}]^2\}, \text{ from}$ which the free energy bias towards locally twisted (cholesteric) packing of segments derives from a term proportional to the volume of average of segment twist, $Tw \equiv \mathbf{Q} \cdot (\nabla \times \mathbf{Q})$ either $Tw_{nem} = \mathbf{Q} \cdot (\nabla \times \mathbf{Q})$ or $Tw_{pol} = \mathbf{p} \cdot (\nabla \times \mathbf{p})$ for respective, nematic and polar cases. Below we show oSCF results for the generic structure of $\mathbf{Q}(\mathbf{x})$ and $Tw_{pol} = \mathbf{p} \cdot (\nabla \times \mathbf{p})$ in ABC triblock networks and helically-ordered cylinders and the twist of segments within domains of different symmetry and handedness.

To model the thermodynamics of complex lattice phases of spherical microdomains, we implement a "diblock foam" model (DFM). This theory is based on a strong-stretching calculation of quasi-spherical domains which occupy the lower symmetry polyhedral cells the tessellate the periodic melt packing. The original theory was derived by Milner and Olmsted, assumes that the shape of the AB interface copies the shape of the low symmetry cell, an approximation which we have shown to be justified in the limit of large conformational asymmetry (stiff outer blocks than inner blocks) and/or larger inner block compositions. In this "polyhedral interface approximation" the free energy density of given sphere packing can be written as $f = \frac{\bar{A}}{R_s} + \bar{I}R_s^2$ where \bar{A} and \bar{I} are the dimensions *area* and 2^{nd} moments of the cells corresponding to the partition, measured in units of the same quantities for spheres which have the same mean volume as the cells, with radius R_s . The two terms in the free energy represent

the AB repulsion at the inter-domain surface in the spheres and the entropic cost of chain stretching to fill the polyhedral cells. Optimizing over the domain volume yields the final free energy of the diblock foam model $f_{min} = (\bar{A}^2 \bar{I})^{1/3}$. Using a customized implementation of developed in the Surface Evolver software, we optimize f_{min} over the shapes of cells that partition space center around points correspond to competing periodic sphere lattices. Via this shape relaxation we compare the free energies of various sphere symmetries, with and without the constraints the spherical domains include the same volume (i.e., in the presence or absence of chain exchange between distinct sphere domains).

Finally, our collaborative study of the mesochiral morphology of experimental triblock networks leverages a methodology developed in collaboration with Prof. Ned Thomas, which extracts the 1D skeletal graphs that thread through the experimental tomographic reconstructions of ordered polymeric networks (see Prasad, Jinnai, Ho, Thomas and Grason, *Soft Matter* 2018, DOI: 10.1039/c8sm00078f). More recently, we have improved this algorithm to exploit topological domain analysis to automatically extract "topologically simple" skeletons without prior assumption about underlying symmetry, scale and orientation of the network domains.

Results and Discussion:

Structural analysis of BCP* network chirality & test of chirality transfer – Building on the development of a new analytic method for quantifying the "handedness" and "degree of chirality" of a periodic network structure developed in our group, efforts in this award period have focused on working closely with the Ho group to apply this analysis to experimental results for network morphologies form by chiral triblock copolymers, PI-PS-PLA*. Again, the critical goal is to assess whether the overall "handedness" of the aDG network morphology formed by these triblocks can be directed by the stereochemistry of the chiral PLA block (PDLA or PLLA), the molecular mechanism of which we explore theoretically as described below. Our method works by fitting the skeletal graph (see Fig. 1A) of tubular network based on 3D intensity data generated by EM tomography (EMT) reconstructions, and then analyze the distribution of "dihedral angles" θ_d between 3-fold junctions in the network (which will show a positive or negative bias for right- and left-handed SG networks). In these experiments, the EMT experiments give spatial distributions of the PI-end block, which is on the opposite network to the PLA block due to its high contrast under staining. Based on iterative efforts between the Grason and Ho groups, significant improvements of the imaging and reconstruction conditions has been achieved over the course of project, leading to now sufficient for resolution on the fairly narrow domains (with roughly ~ 10 nm feature widths) to resolve the SG networks of PI. Additional improvements in the algorithm facilitate numerical extraction of the skeleton without prior bias in term so network symmetry, topology, or orientation, further along for rapid implementation on multiple tomographic data sets. In Fig. 1B-C, we show tomographic reconstruction of the PI domain generated from a 70 nm thick microtome section of the PI-PS-PDLA triblock assembly, whose SAXS pattern and TEM projection confirmed the existence of aDG structure. In Fig. 1D, we show an example of a skeletal graph fit to the network topology from our computational algorithm, and in Fig. 1E, we show a polar histogram plot of the dihedral angle distribution. From this distribution, we find a small, but measureable, signal of left-handed network twist, implying, then that the PDLA domain forms on the (opposing) right-handed SG domain. The weak bias in chirality is in some measure of the limits of resolution of EMT methodology and the reconstruction algorithm, through which microtome sectioning and poor contrast at high tilt angles always lead to angular distortion of the



Fig. 1: In A, a schematic of the inter-node geometry of tubular "struts" in network domains. Three consecutive bo nds (shown in yellow) define the local dihedral angle. In B, a view of a 3D EM-tomography reconstruction of a PI single gyroid domain of a PI-PS-PDLA aDG and C, a 2D slice view transverse to the [110] direction of the c ubic SG. D shows a numerically extracted, topologically-minimal skeletal graph threading through the PI domain. E shows the distribution of inter-node dihedral angles, with a statistical analysis of the local strut chiral order para meter in F showing a statistical bias to left-handed dihedral twist between the nodes.

tubular networks. In order to verify that this left-/right-network bias is in fact directed by the molecular chirality of the PLA end block, we are therefore performing the dihedral analysis of a large set of EMT reconstructions to accumulate sufficient statistics to resolve a weak (for both PLLA and PDLA based samples), the hypothetically, statistically significant bias. Once successful, to our knowledge this will be the first direct experimental test of the relationship between mesochiral network structure and the molecular chirality in any self-assembled polymeric network nanostructure.

The current round of sample preparation and EMT analysis are underway in the next few months, followed by planned skeletal graph analysis for early 2019. If successful, results will be submitted for publication in the spring 2019 timeframe.

Theory of the intra-domain chirality packing: triblock networks – Through this project, we applied oSCF model to understand the connections between mesoscale chirality of the aDG structure formed by triblocks and the segment-scale chiral packing within the tubular single-gyroid (SG) domains. This result provides the first molecular scale mechanism to understand how chirality at the scale of the chain segments and the thermodynamic selection of left- vs. right-handed aDG network morphology based stereochemistry of the constituent chiral PLA block in PI-PS-PLA triblocks studied by the Ho group. Most critically, we have advanced the numerical algorithm to achieve the highest possible spatial resolution for SCF predictions of cubic network morphologies, this is essential because while standard order parameter fields extracted from SCF predictions (specifically the scalar composition fields) require usually less then 100 spatial grid elements per cubic side, the delicate balance between variable twist within BCP domain morphologies requires an unprecedented spatial resolution for accurate SCF predictions, up to 500 grid element per linear direction (shown in Fig. 2A). This allowed us to make the first accurate predictions of the twist distributions and net twist within well-segregated BCP network domains (see Fig. 2B), showing a power law increase of net twist with end/mid-block repulsion strength. The oSCF theory provides a further spatial characterization of the nematic twist within the network domains at the subdomain scale, showing the surprising and novel result for aDG* that even strictly right- or left-handed SG domains possess mixtures of the opposite rotation, with a statistical bias towards a residual twist whose sign is selected by the mesoscopic network symmetry. Notably we find that the predominant twist of the nematic order



Fig. 2: In A, a plot of (A-)segment twist in SG domains of an aDG triblock network of an ABC copolymer fro m oSCF theory, as measured by twist of nematic segment order parameter, Q, here showing the requirement for increased spatial resolution for increased inter-block repulsion. B compares the net (nematic) segment twist vs. block repulsion from the 3 spatial domains, showing that the networks composed of the opposite A and C bloc ks exhibit opposite segment twist, coupled to their enantiomeric SG domain morphologies. C shows the spatial variation of right- (red) vs. left-handed (blue) segment twist within both SG domains of an aDG morphology of ABC triblocks, with D showing a close-up view of the twist within an inter-node strut. E shows a plot of the mesochiral network order parameter, $\chi_2 = \langle \sin(2\theta_d) \rangle$, as function of elongational shear of SG network, the d eformed skeletal graphs of which are shown in G. For comparison, F shows the variation of inter-segment (nem atic) twist from oSCF theory from the SG domain of an aDG triblock network.

parameter winds in the *opposite sense to the dihedral angle* ($\pm 70.5^{\circ}$) between planes formed by nearby 3-fold junctions. Further analysis, has revealed that the sense difference of segment twist analyzed in these different order parameters derives from the distinct patterns of segmental orientation in the core (brush) vs. the interfacial alignment zones. Because the molecular weight dependence of the polar vs. nematic (or apolar) twist is different (nematic twist falls more rapidly with increasing chain length), this result from our oSCF modeling implies the handedness selection of the chiral block (which will be described by both polar and nematic segment interactions) may be reversed with *increases or decreases in molecular weight*, a new prediction for chirality transfer in BCP assemblies.

Beyond the analysis of polar and, nematic twist thermodynamics, we have also carried out an oSCF to systematically explore the relationship between mesoscale chiral structure of a triblock network assembly and the thermodynamic drive associated with twisted packing of segments, as measured by $Tw_{nem} = \mathbf{Q} \cdot (\nabla \times \mathbf{Q})$. Specifically, we have generated a continuous family of chiral networks associated with non-cubic deformations of the aDG network. For example, we show the skeletal graphs of SG networks associates with elongational shears λ along the (100) direction of the initially cubic structure. Fig. 2C shows the variation of the chiral order parameter $\chi_2 = \langle \sin(2\theta_d) \rangle$ which measures the average sense (sign) and magnitude of the "inter-node twist" between 3-fold junctions in the network, characterized by a distribution of dihedral angles, θ_d , showing that deformation (stretching or squashing) of the cubic symmetry (i.e., for $\lambda \neq 1$) continuous lowers the mean inter-node rotation with increasing shear. This raises the basic question, what is the relationship between mesoscale chiral geometry of the SG network (as characterized by the dihedral angle geometry) and the inter-segment twist distribution (as measured by nematic twist) of a non-cubic aDG-like triblock assembly? In Fig. 2D we show the dependence of the average Tw_{nem} as a function of small (~15%) elongational

shears for an aDG-like network at fixed strong segregation and block compositions conditions. We find two important results, first that the net intersegment twist falls away as the network is strongly deformed from cubic symmetry (beyond ~15% deformation), consistent with the dependency of the mesochiral order parameter χ_2 on shear. However, we find that the mean segment twist is not perfectly symmetric about cubic symmetry ($\lambda \neq 1$) and instead has a maximal value of segment twist for slightly elongationally sheared networks (in Fig. 2D this occurs for $\lambda = 1.07$). This result leads to the new prediction that optimal patterns of segment twist, favored by interactions between chiral block segments in triblock network phases, in general, favor non-cubic symmetries. Ongoing work is 1) probing the geometric origin of the favorable non-cubic summetry and 2) mapping out, how this "maximal twist" state depends on thermodynamic factors such as chain composition, inter-block repulsions and molecular weights, in order to understand experimental conditions for realizing this new cubic symmetry breaking in chiral BCP assemblies.

Haven proven the numerical precision requirements for subdomain residual twist predictions, current calculations are underway for theoretical paper (to be submitted in winter 2019) describing the structure and thermodynamics of sub-domain segment twist in mesochiral networks of ABC triblock copolymers and a preliminary phase diagram for the equilibrium window of chirality transfer to network symmetry for comparison the Ho experiments and to guide future experimental/synthetic study.

Generalizing the effect of chirality transfer in block copolymers – Recent studies of diblocks that incorporate blocks with stereopure polymeric backbones have shown that *chirality* has an impact on the self-assembly that falls outside of the traditional BCP paradigm. Notably, solution-cast assembly of polystyrene-b-poly(D or L-lactide) (PS-PDLA or PS-PLLA) diblocks gave rise to form the so-called helical phase (H*), hexagonally packed arrays of helical cylinders whose homochiral helical sense is dictated by monomer stereochemistry. Through this project, a new polymer was synthesized by Ho to test the generality of the formation of mesochiral domains shapes due to chirality at the molecular level, and in particular, to understand how differences in the monomer scale chirality propagate to larger length scales. Poly(cyclohexylglycolide) chiral (PCG)-based block copolymers (BCPs*), poly(benzyl methacrylate)-*b*-poly(D-cyclohexylglycolide) (PBnMA-PDCG) and PBnMA-b-poly(L-cyclohexyl glycolide) (PBnMA-PLCG), were synthesized for purposes of systematic comparison with polylactide (PLA)-based BCPs* (see schematics in Fig. 3), previously shown to exhibit chirality transfer from monomeric unit to the multi-chain domain morphology. Opposite handed PCG helical chains in the enantiomeric BCPs* were identified by the vibrational circular dichroism (VCD) studies revealing of transfer from chiral monomers to chiral intra-chain conformation. We further found VCD evidence of chiral inter-chain interactions, consistent with some amounts of handed skew configurations of PCG segments in a melt state packing, a key ingredient of the chiral mean field theory of BCP* melt theory developed by Grason, and one which has so far not had direct experimental measure. Electron tomography (3D TEM) shown in Fig. 3 chirality at the monomeric and intra-chain level ultimately manifests in the symmetry of microphase-separated, multi-chain morphologies: a helical phase (H*) of hexagonally, ordered, helically-shaped tubular domains whose handedness agrees with the respective monomeric chirality.



Fig. 3: In **A**, the chemical structure of a new chiral BCP, methacrylate)-*b*-poly(D-cyclohexylglycolide) (PBnMA-PDCG), and for comparison, the previously studied class of chiral BCP, polystyrene-*b*-poly(D-lactide) (PS) in **B. C-D (E-F)** show the TEM and SAXS characterization of the helical cylinder (H*) morphology formed by PBnMA-PDCG (PBnMA-PLCG). In **G-H**, TEMT 3D reconstructions are for H* morphologies of PBnMA-PLCG (green) and PBnMA-PDCG (purple) confirm the chirality transfer from the monomeric level of the stereopure PCG blocks to the left- or right-handed screw shape of the domains, giving evidence that the underlying mechanism stabilizing mesohelical domains is generic for multiple chiral polymer block chemistries.

The BCP* studied here, a chiral poly(cyclohexylglycolide) (PCG)-based diblock, is only the second chiral chain chemistry to show chirality transfer to the ultimate mesodomain symmetry, the first being based on chiral poly(lactic acid) (PLA). This is significant because it suggests that the mechanisms underlying chirality transfer to the mesodomain are not unique to a single chemistry. BCPs have been a rich field of study for decades in large part because nearly arbitrary chain chemistries can be mapped onto a relatively small number of coarse grained parameters (number of segments, volume fraction, the Flory-Huggins parameter). In this context, this study is the first to give evidence that the mechanism that promotes chirality transfer from the stereochemistry of a BCP backbone to the mesodomain shape may be also generic, and potentially captured by a relatively small number of additional coarse-grained parameters as proposed by the oSCF model of chiral BCP melts (Zhao, et al. Phys. Rev. Lett. 2013, 110, 058301). Additionally, we show that for chiral PCGs, the stereopure chemical structure promotes intra-chain chiral structure (and ultimately chiral BCP mesodomains), but unlike chiral PLA, this new chiral chemistry does not promote the formation of a crystalline competitor state. Thus, the lack of a crystallization of PCG allows us to test whether the chiral mesodomains form without resorting to kinetic trapping of the BCP in an amorphous state. The unavoidable semi-crystalline state of PLA-based chiral blocks which has so far made it impossible to strictly rule out chiral block crystallization as a driving force for helical domain formation for previously studied chiral BCP. Taken together, the observation of the same mesochiral domain shape in these chemically distinct chiral block chemistries both suggests the principles underlying the formation of this phase (not unlike the canonical phases of achiral BCPs) are generic, and further provides the first systematic comparison between two systems exhibiting chirality transfer in BCP, a first step in establishing "chirality" as a new and generic axis of the BCP assembly parameter space. Comparison of different measures of chirality at the monomer scale for PLA and PCG (ECD spectra) facilitate a comparison to mean-field theory results for chiral diblock copolymer melts, and suggest that the enhanced thermodynamic stability of the mesochiral H* morphology may be attributed to the relatively stronger chiral inter-segment forces, ultimately tracing from the effects of a bulkier chiral side group on its main chain.

A manuscript on this work entitled "Generalizing the Effects of Chirality on Block Copolymer Assembly" was submitted to PNAS in Summer 2018. The first round of review received generally favorable comments from reviews and the editor. A revised version has been resubmitted and is now under consideration.

Geometric theory of Frank Kasper phases in diblock melts – In this new research thrust, we have implemented a new geometric "diblock foam" model (DFM) to investigate the mechanism underlying the stability of complex Frank Kasper (FK) sphere phases recently observed by Bates and coworkers in melts of relatively low molecular weight PI-PLA diblocks. Relative to many standard diblock systems, PI-PLA chains have a significant "conformational" (or stiffness) asymmetry between the constituent blocks. In particular, our aim is to understand the geometric factors that select one lattice over others. It is currently thought that the sigma lattice is thermodynamically stable at low temperature, but a range of other related structures, including the A15, C14 and C15 lattice have also been reported. Heuristic arguments have been advanced by Bates and others to understand why these complex (large unit cell) lattices form focusing on the lattice symmetries whose polyhedral Voronoi cells are most "spherical" (see Fig. 4). Our DFM has the unique capability to directly model the free energy of competing sphere lattices in terms of the microdomain "cell geometry", and discern precisely which thermodynamic drive is most significant in selecting the optimal lattice, minimal area of the partition, and minimal stretching of the chains within the polyhedral domains.

Moreover, we have applied the oSCF theory to probe the orientational order parameter within the sphere phases (see **Fig. 4E**) as a function of conformational asymmetry and revealed that a new sub-unit cell domain shape transition takes place (from discoidal to quasi-polyhedral domains) that underlies the stability of FK phases over canonical lattice phase of BCP (e.g. BCC, FCC).

A manuscript on this work (in collaboration with F. S. Bates and K. Dorfman) has been published in PNAS in September 2018 (DOI: 10.1073/pnas.1809655115).



Fig. 4: In **A**, a schematic of chain configurations of conformationally asymmetric diblocks in an ordered of spher ical domains. **B** shows the cellular geometry of C15 Frank Kasper (FK) phase used in the "diblock foam mode I" (DFM) which optimizes the free energy in terms of geometric measures of cell sphericity. **C** shows the res ults of DFM for competing phases, indicating the relaxation of spherical domains to unequal volumes (in **D**) un derlies the stability of the equilibrium *sigma* lattice. In **E**, the oSCF analysis of the subdomain morphologies o f Z14 cells of the A15 phase, showing a transition from "discoidal" (conformationally-symmetric) to "quasi-poly hedral" (conformationally-asymmetric) domain shapes, which triggers the transition from canonical (e.g. BCC) sp here lattices to stable FK lattices.

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:

a) papers published in peer-reviewed journals,

- A. Reddy, M. B. Buckley, A. Arora, F. S. Bates, K. D. Dorfman and G. M. Grason, "Stable Frank-Kasper phases of self-assembled, soft matter spheres", *Proceedings of the National Academy of Sciences USA* **115**, 10233-10238 (2018), DOI: 10.1073/pnas.1809655115.
- T. Wen and R.-M. Ho, "Effects of the Chiral Interface and Orientation-Dependent Segment Interactions on Twisting of Self-Assembled Block Copolymers," *ACS MacroLetters* **6**, 370 (2017), DOI: 10.1021/acsmacrolett.7b00138.

b) papers published in non-peer-reviewed journals or in conference proceedings,

None.

- c) conference presentations,
 - Ishan Prasad, GM Grason, "Theory of Chirality Transfer in Block Copolymer Melts", contributed talk at *APS March Meeting*, Baltimore, MD, March 2016.
 - Ishan Prasad, GM Grason, "Intra-domain Orientation in Block Copolymer Melts", contributed poster presentation at the *Gordon Research Conference on Polymer Physics*, Mt. Holyoke College, South Amherst, MA, July 2016.
 - GM Grason, "Intradomain textures and chirality transfer in block copolymer melts", invited talk at *Greater Boston area Statistical Mechanics Meeting*, Waltham, MA, October 2016.
 - GM Grason, "Block copolymers beneath the surface: Intradomain textures and mesochiral morphologies", invited *PSE 50 Japan* a satellite conference of the 2016 *International Polymer Conference*, Kitakyushu, Japan, December 2016.
 - Abhiram Reddy, MB Buckley, A Arora, FS Bates, KD Dorfman, GM Grason, "Superlattices of squishable, self-assembled spheres: How lattice cell geometry shapes thermodynamics", contributed poster at *Gordon Research Conference on Soft Matter*, Colby-Sawyer College, New London, NH, August 2017.
 - GM Grason, "Block copolymers beneath the surface: Intradomain textures and chirality transfer to mesodomains", invited talk at *ACS Fall Meeting*, Washington D.C., August 2017.
 - Abhiram Reddy, MB Buckley, A Arora, FS Bates, KD Dorfman, GM Grason, "Superlattices of squishable, self-assembled spheres: How lattice cell geometry shapes thermodynamics", contributed talk at *APS March Meeting*, Los Angeles, CA, March 2018.

- Abhiram Reddy, MB Buckley, A Arora, FS Bates, KD Dorfman, GM Grason, "Stable Frank-Kasper Phases of Self-Assembled, Soft Matter Spheres", contributed talk at *MRS Fall Meeting*, Boston, MA, November 2018.
- RM Ho, "Homochiral Evolution in Self-Assembled Chiral Block Copolymers and Polymers", keynote talk at *International Polymer Conference* 2018, Hiroshima, Japan, December 2018
- RM Ho, "Universal Effects of Chirality on Self-Assembly of Block Copolymers", keynote talk at *International Symposium for Soft Matter Science and Technology*, Chengdu, China, November 2018
- RM Ho, "Nanonetwork materials from templated syntheses using block copolymer templates", invited talk at *ACS National Meeting*, 2018, Boston, MA, USA, August 2018
- RM Ho, "Universal Effects of Chirality on Self-Assembly of Block Copolymers", keynote talk at *4th Molecular Chirality Asia*, Harbin, China, July 2018

RM Ho, "Well-Ordered Nanonetwork Materials from Templating of Self-Assembled Chiral Block Copolymers", invited talk at *International Membrane Conference in Taiwan*, Chungli, Taiwan, June 2018

- RM Ho, "Well-Ordered Nanonetwork Materials from Templating of Self-Assembled Chiral Block Copolymers", invited talk at *Pacific Polymer Conference 2017*, Xiamen, China, December 2017
- RM Ho, "Homochiral Evolution in Self-Assembled Chiral Polymers and Block Copolymers" invited talk at *IUPAC-FAPS 2017 Polymer Congress*, Jeju Island, Korea Oct 2017
- RM Ho, "Homochiral Evolution in Self-Assembled Chiral Polymers and Block Copolymers" invited talk at *Chirality 2017*, Tokyo, Japan, July 2017
- d) manuscripts submitted but not yet published, and
 - H.-F. Wang, W.-Ch. Hsu, K.-C. Yang, J.-Y. Lee, J.-T. Hsu, G. M. Grason, E. L. Thomas, J.-C. Tsai and R.-M. Ho, "Generalizing the Effects of Chirality on Block Copolymer Assembly", *Proceedings of the National Academy of Sciences USA (resubmitted after first round of review, 2018).*

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

Visit for AFRL Wright Patterson in March 2017 (hosted by Dr. R. Pachter)– Joint visit of Grason and Ho present ongoing collaborative work, meet with AFRL researchers (in "soft materials" and "photonic materials" groups) to explore avenues for possible collaboration.