RX20-21

1. **Research Title:** Identification of Local Structure Evolution in Selective Heating of Tailored Pre-ceramic Polymers
2. **Individual Sponsor:**

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3. **Academic Area/Field and Education Level**
Materials Science and Engineering, Chemical Engineering, Chemistry, Physics, or equivalent (MS or PhD level)
4. **Objectives:**

The objective of this effort is to develop a structure-processing-property relationship through selective heating during the polymerization and conversion stages of preceramic polymers. Of particular interest is developing an understanding on how local structure evolves during the polymerization of the preceramic polymer into different phases and domains in the presence of certain filler particles and electromagnetic radiation. This will provide insight into how selective heating and other polymerization pathways can be utilize to utilize preceramic polymers to create inorganic glasses and ceramics with targeted compositions, phases, and functionalities.

5. **Description:**

Preceramic polymers (PcPs) are precursor materials made up of organic-inorganic, usually organosilicon, polymers that under proper thermal treatment can produced a ceramic material. One of the main benefits of using these polymers is they can often be processed and shaped into a variety of form factors that are not achievable through conventional powder sintering. The different pathways of polymerization, pyrolysis, and conversion of the polymer on the local structure and its evolution into an inorganic glass and eventual crystalline ceramic is an often ignored or overlooked aspect of these materials. There is a fundamental need for developing controlled, reproducible polymerization mechanisms of ceramics using preceramic polymers.

Conventional high-temperature synthesis of preceramic polymer typically involves subjecting the precursors to identical heating conditions without selectivity. The inhomogeneity of materials in preceramic polymerization strategies with nanostructured in-fill templates allow for opportunities to selectively heat and control selected growth mechanisms. This topic will investigate selective heating strategies with electromagnetic radiation (i.e. microwave-assisted heating) to accelerate production of targeted growth pathways of tailored preceramic polymers. By tuning the dielectric properties of the nanostructured in-fills, the templated material can be used as the microwave susceptor or cast as inactive species. Depending on if the filler is active/reactive with the preceramic polymer during conversion, this can result in new phases or a change in the dielectric properties as the structure converts into a ceramic.

Subsequently, there can be an absence or presence of a synergistic interplay[1] between precursors due to their materials properties. The cross-linking mechanism can be tracked with collection of *in-situ*

total X-ray scattering to calculate the pair distribution functions (PDF). This method has had little application to preceramic polymers but offers a wealth of insight into the conversion process. The PDF method considers Bragg diffraction scattering contributions from long-range periodic ordering of atoms in a lattice as well as the diffuse scattering from atomic disorder.[2] The PDF method has been particularly useful for studies involving systems such as amorphous materials,[3] nanostructured materials,[4–8] and liquids.[9] These systems do not possess long range atomic ordering but do possess local structure, up to approximately 6 Å. The pair distribution function, *G(r)* (Equation (1)), is the Fourier transform of the structure factor, *S(q)*, is a real-space histogram of the distribution of atomic positions. From the PDF, information regarding bond lengths and particle size can be deduced. Quantitative analysis of the coordination number, *n*, can be obtained by Equation (2) in which ρ_0 is the average density. Fundamental insights gained from this advanced characterization technique will create foundational knowledge of polymerization pathways of designer preceramic polymers with targeted functionalities.

$$\mathrm{G(r)} = \frac{2}{\pi}\int_{q_{min}}^{q_{max}} Q(S(q)-1)\sin(qr)dq \quad (1)$$

$$\mathrm{n} = 4\pi\rho_0 \int_{r_1}^{r_2} r^2 G(r)dr \quad (2)$$

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6. Research Classification/Restrictions:

This research is unclassified

7. Eligible Research Institutions:

DAGSI (Wright State University, AFIT, Ohio State University, University of Dayton, Miami University, Ohio University, University of Cincinnati, and University of Akron)

NOTE: Topics submitted to DAGSI must be approved for public release. Need PA Approval #