Microphase Separation Technique Mediated SiCN Ceramics: A Method for Mesostructuring of Polymer Derived SiCN Ceramics

This Article is Dedicated to Prof. Dr. Rhett Kempe on the occasion of his 60th birthday

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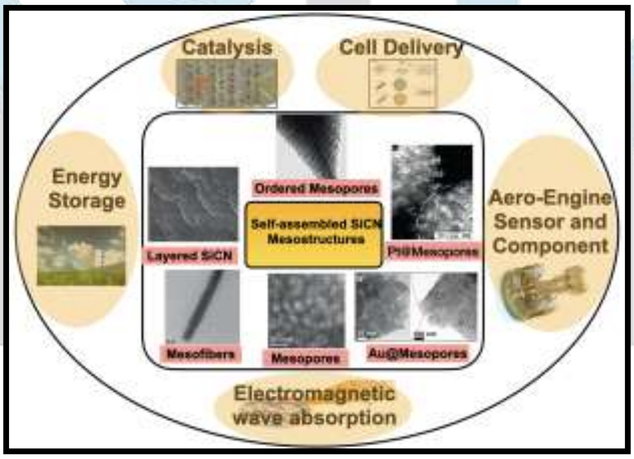
***Abstract*— Polymer-derived ceramics (PDCs) are widely utilised across various fields, including engineering, science, and medicine. The ability to enhance their surface properties through mesostructuring transforms bulk PDCs into advanced materials with superior functionalities. Among PDCs, silicon carbonitride (SiCN) stands out as a non-oxide ceramic with exceptional properties such as high-temperature resistance, chemical inertness, mechanical stress resistance, and semiconducting capability. This review focuses on mesostructuring of SiCN ceramics through microphase separation of direct inorganic precursor-block-organic copolymers and other significant approaches. This approach is particularly advantageous, as the resulting mesostructured SiCN ceramics can be precisely tuned by adjusting polymer ratios, controlling thermal cross-linking, and implementing programmed pyrolysis. Furthermore, this method enables the synthesis of mesostructured SiCN-supported metal nanoparticles for catalysis. By incorporating metal precursors into amphiphilic copolymers prior to microphase separation and pyrolysis, a convenient and efficient route to catalytic materials is established. This review provides a comprehensive discussion of existing research on mesostructured SiCN ceramics and**



their supported catalysts, with a particular emphasis on self-assembly and microphase separation techniques.

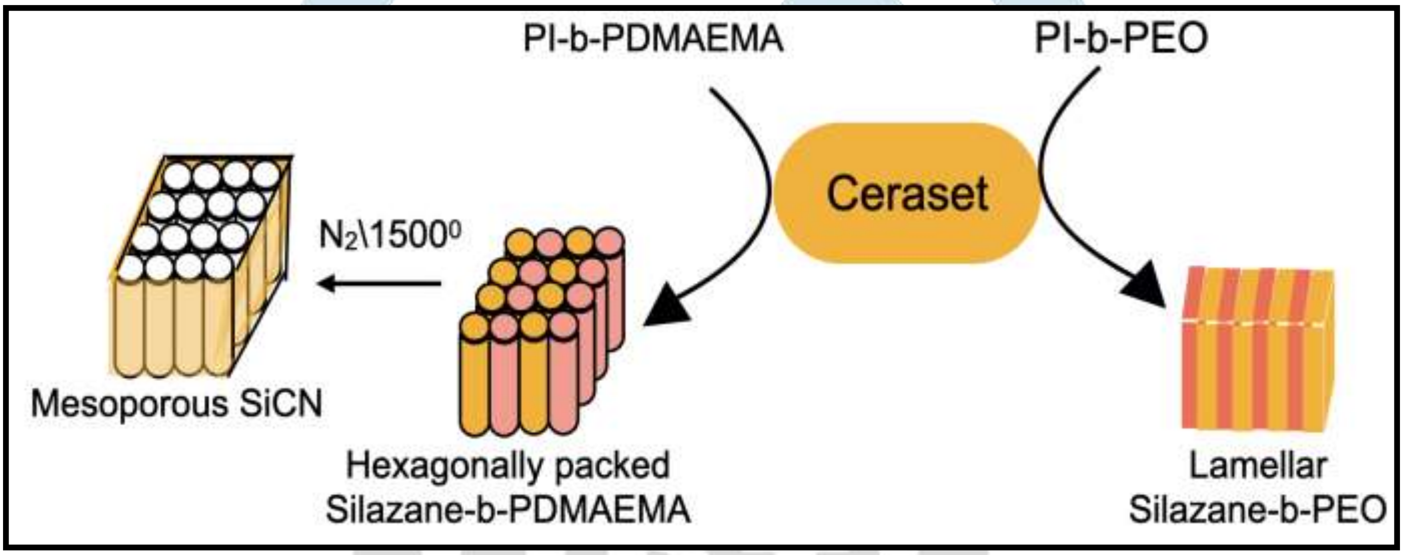
Self-assembled SiCN Ceramics • Mesoporous SiCN catalyst • Mesostructured SiCN • Microphase separated SiCN ceramics.

I. INTRODUCTION (HEADING 1)

Novel polymer derived silicon based materials under the mesoscale regime (5-50nm) are much anticipated in many industries as they have capable of aligning with chip level scale and genetic arrays.[1] Within the broad applications aspects of polymer derived ceramics[2] (PDCs), siliconcorbonitride (SiCN) is of particular interest due to it's wide range of applications in catalysis[3], energy storage[4], aero-engine sensor[5], elacromagnatic wave absorption devices[6] and living cell delivery[7]. These ceramics are particularly exceptional high temparature withstanding materials due to the amorphous phases and covalently linked network surface. In general, synthesis of nanoscale SiCN is possible under broad inventory of techniques such as lithograhy, PDMS molding, sputtering, template inversion and so on. Particularly, the self-assambly[8] of mesoscale materials using microphase separation[9] of copolymers offers wide range of mesostructured ceramics materials[10] due to the repulsive strength of the linked polymers and amphiphilic incompatibility between the linked copolymers.[11] However, only few specimens exists in the mesostructured form of SiCN due to the limited synthetic approaches namely block copolymer as structural directing agent, sacrificial template for the increased structure, and direct copolymer micro-phase separation. Bringing the uniformed morphology within the sample is a big hurdle due to the presence of ternary phases exists in the sample. Among many difficulties in producing mesostructured SiCN, choosing ceramic precursor, dissimilar other block, ratio of the blocks, block chain length, cross linking temperature condition, retaining the microphase separated structure within the green body and figuring out the controlled pyrolysis program are challenging task to retain the phase separated structure through out the entire process. This same technique also be applicable for the synthesis of mesostructured SiCN supported metal nanoparticles for catalysis. In addition to the above mentioned steps, a metal precursor is added before the formation of green body that allows the transmetallation from the metal precursor to SiCN precursor and stabilised by the N atom of the SiCN network leading to the synthesis of mesostructured M@SiCN catalyst. In this mini review, most of the techniques used for the synthesis of nanostructured SiCN ceramics will be presented and advantages of microphase separation technique in particular will be highlighted for the mesostructuring of SiCN and M@SiCN exclusively.

Copolymers as structural directing agent

The Wiesner group pioneered this approach for the synthesis of mesostructured SiCN ceramics by adding ceraset, an oligomer of silazane, to the copolymer with having one block compatible with polysilazane precursor. In the earlier article, poly(isoprene-block-ethyleneoxide) (PI-b-PEO) copolymer were used as structural directing agent that cooperatively self-assembled to form lamellar mesostrucred silazane-b-PEO.[12] The resultant morphology is analysed and confirmed using transition electron microscopy (TEM) and small angle X-ray spectroscopy (SAXS). In this work, pyrolysis part, which converts the silazane-b-PEO to mesostructured SiCN, is not reported rather mentioned as the basis for the synthesis of mesostructured SiCN by preserving the morphology. Later on, the same group published an article reporting the pyrolysis part and proved the mesosturctured SiCN is possible via this approach and laid the basis for the future. In this article, poly(isoprene-block-dimethylamino ethyl methacrylate) (PI-b-PDMAEMA) is used as structural directing agent blending with ceraset followed by the formation of hexagonal morphology at green body stage that lead to mesoporous SiCN ceramics upon pyrolysis.[13] The resultant morphologies before and after pyrolysis were confirmed by SAXS and TEM respectively. Interestingly green body synthesised in both of the above mentioned articles results under mesoscale



regime and created a strong approach for the synthesis of mesostructured SiCN ceramics.

Figure 1. Schematic diagram representing the copolymers as structural directing agent for the mesostructuring of SiCN precursor polymer.

Sacrificial template Method

Towards aiming for the utilisation in high temperature fuel reforming, microporous SiCN ceramics is synthesised by Kim and Keins using capillary pore filtration of SiCN precursor within the void space of the self-assembled polystyrene or silica nanoparticles.[14] In this approach, PDMS mold is used as template assembly chamber in the first step and confirmed the packing of spheres using scanning electron microcopy (SEM). In the second step, using capillary action a KiON ceraset polyvinylsilazane as precursor SiCN is infiltrated followed by the pyrolysis at 1200 ^{0}C for two hours to yield microporous SiCN upon subsequent etching of PS or SiO_2. This was the only known sacrificial template approach for the synthesis of macroporous SiCN ceramics until the alternative approach recently reported for the synthesis of mesoporous SiCN ceramics by the group of Kempe. This group have simplified the sacrificial template method to a single pot approach from the instrumental and complicated two step process.[15] Herein polystyrene of about 60 nm solutions of partial positive and negative charged PS, aiming to adjust the zeta potential for the well dispersion in the solution of pre ceramic precursor, is mixed well with SiCN precursor solution and cross linked followed by pyrolysis at 900-1100 ^{0}C. The resultant mesoporous SiCN is analysed using SEM and TEM and confirmed the range of pore size within the range of 4-12 nm. Interestingly, Wiesner group have reported the fabrication of mesoporous SiCN supported platinum nanoparticles catalyst using PI-b-PDMAEMA copolymer as structural directing agent within the PDMS mold packed by polystyrene (PS) spheres.[16] The PS spheres packed in the PDMS mold act as sacrificial agent as well as providing the void space for the infiltration of PI-b-PDMAEMA, precursor silazane, and platinum complex. The resultant Pt@SiCN framework after pyrolysis confirms the hierarchal porous structure from the contribution of macro scale PS spheres and PI-b-PDMAEMA/silazane self assembled mesopores. This method is still an elegant and sophisticated approach to synthesise mesoporous Pt@SiCN catalyst.

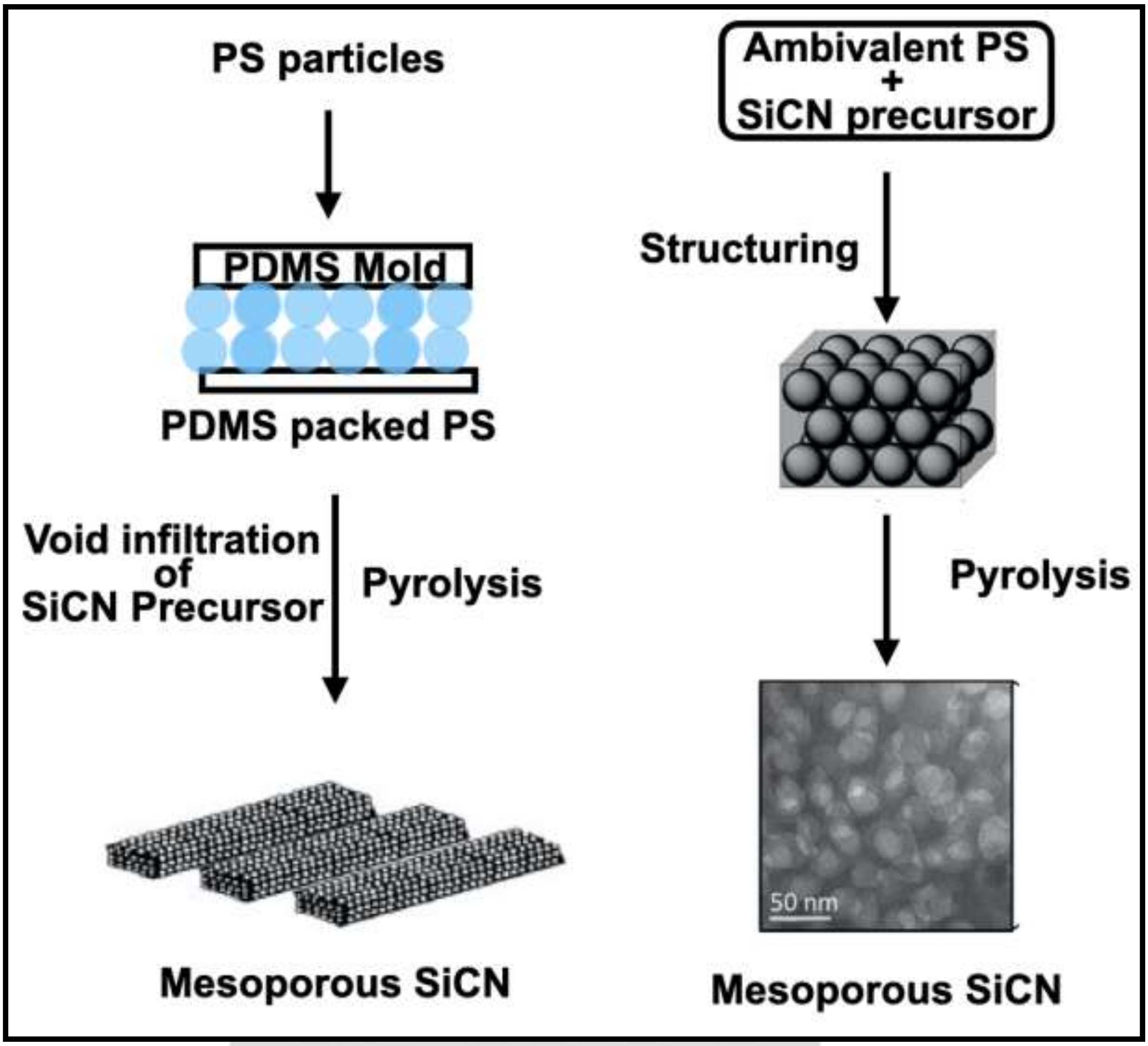


Figure 2. Depiction of the scaffold template aided mesostructuring of SiCN precursor polymer through void infiltration and direct structuring methods.

Direct copolymer microphase separation

None of the previously discussed methods were used direct silazane polymer linked copolymers as precursor for the synthesis of mesostructured SiCN ceramics as this copolymers have many advantages in formation of self-assembled morphologies in a simplified approach. First in the place, Kim group have reported the synthesis of polyvinylsilazane-b-polystyrene (PVSZ-b-PS), a direct precursor linked inorganic-organic copolymer, by reversible addition fragmentation chain transfer (RAFT) polymerisation.[17] Due to the tendency of this copolymer to undergo self assembly and form mesoscale morphologies, upon pyrolysis of this copolymer leaves the inorganic precursor block in the form of pore walls and organic block in the form of pores to yield mesoporous SiCN ceramics. Followed by this approach, the same group have have tuned the approach by using lithographic technique for the synthesis of thin film mesoporous SiCN ceramics with having ~6 nm poresize.[18] In this approach photoresistble PVSZ-b-PMMA synthesised by using RAFT polymerisation with subsequent functionalisation of methacrylate group. After attaining self assembled morphology, the resultant structure is exposed to the UV light degradation of PMMA block for the successful synthesis of mesoporous SiCN ceramics. This approach is still not a viable method for the bulk synthesis of mesoporous SiCN for the industrial application. Notably, Yang *et al* contributed to this approach for the synthesis of hallospheare SiCN by RAFT polymerised PVSZ-b-PS followed by self-assembled miscall morphology leading to mesostructured SiCN ceramics.[19] Later on a significant modification to this approach is made by Pillai *et al* belongs to the Kempe group in terms of linking the precursor inorganic block to a polyethylene with hydroxyl end functional group[20] block, a simplified version of making inorganic-organic copolymer.[21] In this method, copolymer of PVSZ-b-PE with different ratios is microphase separated into two different morphologies in which lamellar morphology results mesolayerd SiCN and the other morphology results mesofibers SiCN ceramics. The whole process is based on the copolymer formation, microphase separation, and programmed pyrolysis steps. The resultant copolymer morphologies before and after pyrolysis are confirmed by TEM and SEM analysis. The mesofibers reported in this article is not reported elsewhere to the best of knowledge using this method. The same method with three consecutive steps is further utilised in the preparation of mesoporous SiCN supported gold nanoparticles (Au@SiCN) by simple modification of injecting aminopyridinato gold complex to the PVSZ-b-PE solution.[22] Advantage of synthesising mesoporous Au@SiCN using this approach is by preventing the agglomeration of Au nanoparticles during the high temperature pyrolysis which is due to the sturdy SiCN pore walls and N atom present in the SiCN network frame.[23] The synthesised Au@SiCN catalyst is confirmed and analysed by TEM, SEM, and powder XRD techniques.

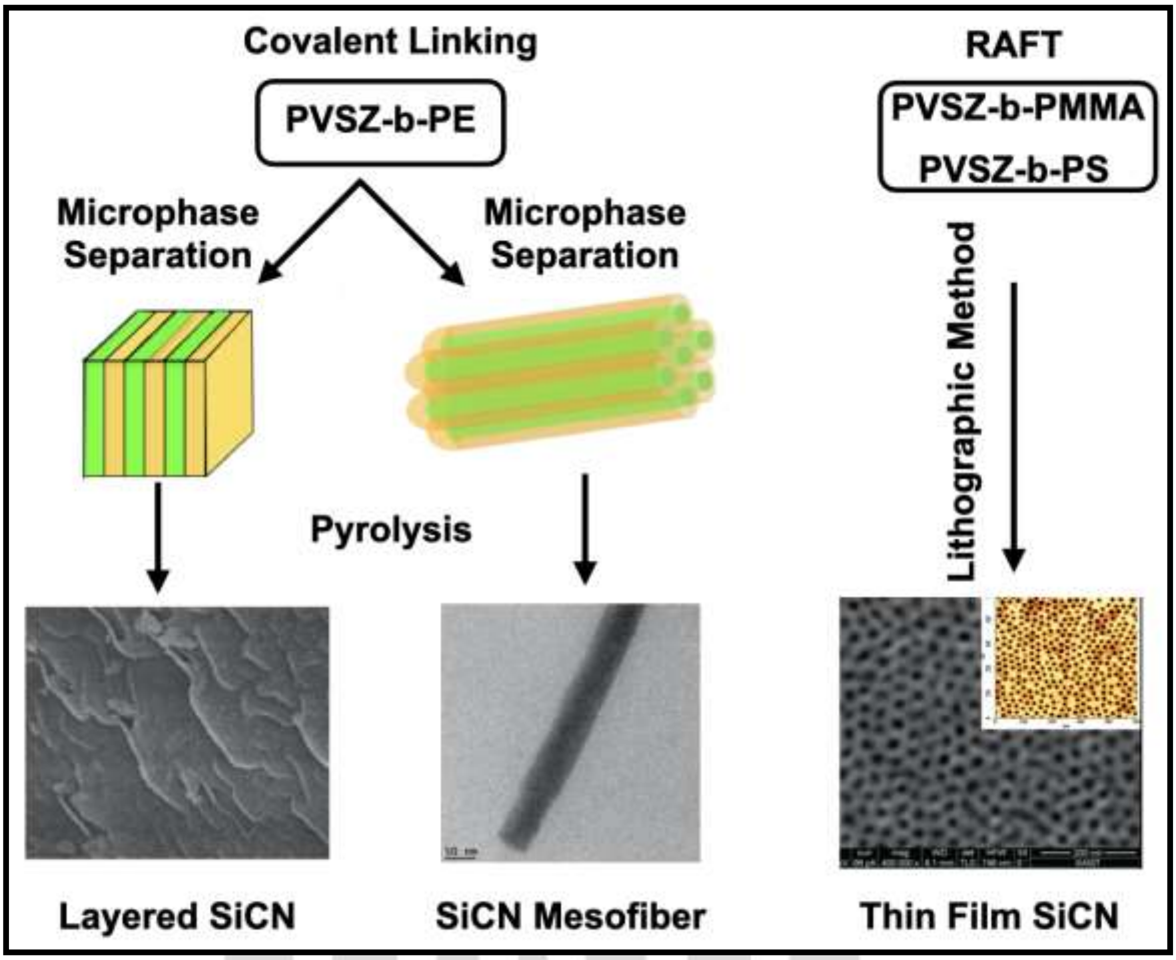


Figure 3. Schematic diagram representing the mesostructuring of SiCN ceramics via direct copolymer microphase separation technique.

Discussion and Conclusions

The microphase separation technique has emerged as a promising method for achieving mesostructuring in polymer-derived ceramics (PDCs), particularly for siliconcarbonitride (SiCN) ceramics. The reviewed studies highlight the effectiveness of this approach in tailoring the morphology and porosity of SiCN ceramics by manipulating polymer ratios, thermal treatment conditions, and controlled pyrolysis. This technique has demonstrated versatility, not only in the fabrication of mesostructured SiCN but also in the synthesis of supported metal catalysts such as M@SiCN. These findings establish microphase separation as a powerful and scalable route for designing high-performance materials with enhanced surface properties.

The major implications of this research extend across various fields, including catalysis, energy storage, and biomedical applications. The ability to fine-tune mesostructures allows for the optimization of SiCN properties, making them suitable for use as catalytic supports, electrodes in batteries, biosensors, and advanced structural components. The development of mesoporous SiCN-supported metal nanoparticles further expands the application scope, particularly in heterogeneous catalysis, where high surface area and stability are crucial.

Despite these advancements, several knowledge gaps remain. The scalability of the microphase separation technique for industrial applications is still a challenge. Further research is needed to explore the long-term stability of mesostructured SiCN ceramics under extreme conditions, as well as their compatibility with functional coatings and composite materials. Additionally, the interactions between the polymer blocks during phase separation and their influence on the final ceramic structure require deeper investigation. Future directions in this field may include the integration of computational modeling to predict phase separation behaviour and optimise polymer design. Advances in lithographic techniques and additive manufacturing could further refine the structural control of mesostructured SiCN ceramics. Additionally, exploring alternative polymer precursors and porogens may lead to novel mesostructured ceramic materials with enhanced properties. The emergence of hybrid materials combining SiCN ceramics with other functional nanomaterials also presents exciting possibilities for next-generation applications in nanotechnology and materials science.

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