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Boron Nitride Ceramics from Molecular Precursor: Synthesis, Properties and Applications

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Hexagonal boron nitride (h-BN) attracts considerable interest according to its structure similar to carbon graphite while it displays different properties which offer attractivity for environmental and green technologies. The polar nature of the B-N bond in sp^2-bonded BN makes it a wide band gap insulator with different chemistry on its surface and particular physical and chemical properties such as a high thermal conductivity, a high temperature stability, a high resistance to corrosion and oxidation and a strong UV emission. It is chemically inert, nontoxic and it has good environmental compatibility. h-BN also has enhanced physisorption properties due to the dipolar fields near its surface. Such properties are closely dependent on the processing method. Bottom-up approaches consist in transforming molecular precursors into non-oxide ceramics under retention of the structural units which are inherent to the precursor molecule. The purpose of the present review is to give an up-to-date overview on the most recent achievements in the preparation of h-BN from borazine-based molecular single-source precursors including borazine and 2,4,6-trichloroborazine through both vapor phase syntheses and methods in liquid/solid-state involving polymeric intermediates we called the Polymer-Derived Ceramics (PDCs) route. In particular, the effect of the chemistry, composition and architecture of the borazine-based precursors and the derived polymers, on the shaping ability as well as on the properties of h-BN is particularly highlighted.

Keywords: boron nitride; borazine; 2,4,6-trichloroborazine, polyborazylene, poly[aminoborazine], vapor phase synthesis, shaping, pyrolysis.

A Introduction

Common oxide ceramics such as silica and alumina are largely dominating the ceramic field, and the understanding of their chemistry, processing and properties is consequently well developed. Since three decades, there was a growing interest in non-oxide ceramics, particularly carbides, mainly for thermostructural and aeropace applications, more recently focused on nitrides for energy applications.[1] In nitrides, the nitrogen atom is combined with an element of similar or lower electronegativity such as boron, silicon or most of the metals. Nitrides contain the nitride ion N^{3-} and two categories can be distinguished: the transition metal series of the periodic table and the ionic-covalent family. In the latter, the interest for boron nitride (BN) grew during the past decades in relation with its unique combination of key properties. BN, isoelectronic and isostructural to its carbon counterpart, is a III-V material which exists in four polymorphic forms: two dense sp^3 hybridization (cubic BN (c-BN) and wurtzite BN (w-BN)) and two graphite-like sp^2 hybridization (hexagonal BN (h-BN) and rhombohedral BN (r-BN)). Each polymorph exhibits special properties which are summarize hereafter. In addition, fullerene-like BN and single-/multi-walled BN nanotubes, which are particular structures, can be considered as the fifth and sixth crystalline polymorphic phases.[2] On the other hand, graphene-like BN nanosheets can be considered as belonging to the hexagonal polymorph with the peculiarity to display a very high specific surface area.[3]

Wentorf reported the preparation of c-BN by high temperature and pressure in 1957 similar to diamond elaboration.[4] The cubic form exhibits properties similar to those of diamond with a greater resistance against oxidation. The wurtzite form, originally prepared by Bundy and Wentorf, [5], is a super hard form of BN with properties close to those of c-BN. With its polycrystalline structure, w-BN provides superior cutting properties, high shock resistance, stress induced shear transformation responsible for toughening.[6] The graphite-like sp^2 hybridization labelled h-BN has been the topic of a lot of studies, which can be mainly attributed to its relative ease of synthesis and to its layered structure which consists of strong in-plane bonds (covalent type) and much weaker bonds (Van

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Der Waals type) in the third dimension as described below in more details.[7] Its layered structure provides useful properties and its modification by various post-synthesis treatments which has attracted a lot of attention for many years extending, therefore, the applications of h-BN.[8-15] Indeed, since the discovery of carbon nanotubes, porous carbon (including ordered mesoporous carbon, carbon foams, carbon aerogels) and more recently graphene coupled with a significant increase of the number of emerging applications in environmental and green technologies, the research into the fundamental science of its h-BN analogue has been also intensified.[8-20] This has been also facilitated by the ability to better tailor now the nanostructures of these layered materials, to easier handle individual layers and to improve the characterization of these materials. According to its fascinating characteristics and to its huge potentialities, h-BN is the subject of the present paper.

h-BN was synthesized originally in 1842 by Balmain[21] and its structural arrangement was proposed for the first time in 1952 by Pease.[22]. He reported lattice parameters of 2.504 Å (for a) and 6.661 Å (for c). The polar nature of the B-N bond in sp^2-bonded BN makes it a wide band gap insulator with different chemistry on its surface and exciting physical and chemical properties including, high thermal conductivity, high temperature stability and high resistance to corrosion and oxidation and strong UV emission. It is chemically inert, nontoxic and it has good environmental compatibility. BN also displays enhanced physisorption properties due to the dipolar fields near its surface. As porous, BN exhibits unique physical and chemical properties for applications in various fields especially those related to adsorption like gaseous uptake, pollutant adsorption and catalyst supports as well as those related to DNA translocation.[23-29] However, such properties are closely dependent on the structural and textural characteristics of h-BN as well as the shape which, in fact, are affected even determined by the material synthesis procedure applied to prepare h-BN. Within this context, proper synthesis routes and advanced structural designs are still among the great challenges for preparing h-BN with tuned shapes and tailored properties.

Similarly to a large number of ceramics, various routes have been used for the synthesis of h-BN. The typical route includes the powder metallurgy technologies where BN is generally obtained by reaction of boric oxide with ammonia (T > 900°C), or with organic nitrogen compounds such as melamine/urea (T > 1000°C), or by nitridation of calcium hexaboride in the presence of boric oxide (T > 1500°C).[30,31] However, one of the alternative strategies to reach some of the aforementioned properties of h-BN on the device level is to control the structure of materials at very small length scales in an early stage of the fabrication leading to the emergence of bottom-up approaches. The methods in gas (vapor) phase such as the chemical vapor deposition (CVD) or spray-pyrolysis methods, from volatile boron and/or nitrogen-containing precursors,[32,33] and the methods in liquid and/or solid state involving borazine-based polymers are alternative preparative methods to design precursor-derived h-BN in a way not known through conventional processes.[34-42] The purpose of the present paper is to give an up-to-date overview on the most recent achievements in the preparation of h-BN from borazine-based molecular single-source precursors. We will first address the general procedures to prepare non-oxide ceramics from molecular and polymeric precursors, then, in a second part, we will discuss on the synthesis of borazine-based molecular single-source precursors and their use in the vapour phase syntheses. The third part will present the synthesis of polymeric intermediates which offer shaping capabilities to form h-BN in various shapes which are the object of specific studies conducted by our research group. The properties of obtained h-BN will be discussed in each section of the present paper.

B Non-oxide ceramics by bottom-up approaches

The idea behind the chemical synthesis of non-oxide ceramics is to transform molecular precursors into materials with the retention of the structural units, which are the basic pattern of the precursor molecule and also to form an integral part of the solid-state structure (Fig. 1).

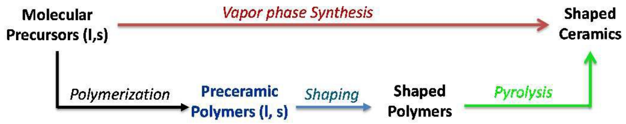

Figure 1. The Precursor-Derived Non-Oxide Ceramics routes.

The vapor-phase synthesis of non-oxide ceramics is a one-step fabrication method which involves vaporization of the molecular precursor and gas phase reactions followed by nucleation/condensation/growth from the vapor phase. The vapor may be generated by thermal, laser, electron beam, etc. Different sources of energy can be used to decompose the precursor such as microwave plasma, laser pyrolysis, laser photolysis, combustion flame, etc. The range of these processes is very wide. The most common/typical applications are the CVD (Chemical Vapor Deposition), ALD (Atomic Layer Deposition), MLD (Molecular Layer Deposition), spray CVD and spray pyrolysis processes to form nano-objects, thin films, porous materials, composite materials … Such techniques can be also applied for surface modification, cleaning and functionalization. The method in liquid and/or solid phase to generate non-oxide ceramics is called the Polymer-Derived Ceramics (PDCs) route and uses polymeric intermediates commonly called preceramic polymers.

The preceramic polymer concept dates back to 1956–1957 when Fritz *et al.*[43] then Yajima *et al.*[44] reported the first polycarbosilane-derived silicon carbide (SiC). These findings marked the beginning of extensive research on preceramic polymers, which led to the development of silicon nitride (Si_3N_4) and SiC fibers. Today the most common Polymer-Derived Ceramics (PDCs) procedure is still based on the process published by Japanese researchers in 1976.[44] The development of this scientific knowledge requires an interdisciplinary base that spans the fields of molecular chemistry, inorganic chemistry, polymer chemistry, materials science and engineering. The major advantages of this concept are the relatively easy control of the composition at atomic level as well as the elemental homogeneity of the final material. Furthermore, the polymer can be easily shaped using the vast variety of shaping techniques developed for processing organic polymers and then converted into ceramics by heat-treatment typically above 800°C.[45] Also and unlike traditional method, it is possible to produce amorphous ceramics with an improved hardness by playing with the heat-treatment final temperature.

As an illustration, the PDCs route offers an easy way to synthesize ceramic fibers,[44,46] films (dense[47] or microporous (*i.e* membranes)[48]), porous materials (ordered mesoporous powders, foams…)[49-55] which cannot be produced using powder technology. Furthermore, the extension of the PDCs route to a wider range of ceramic compositions (nanocomposites) can be achieved *via* the modification of the polymers at the nano-scale, *i.e.*, on their reaction with lower molecular weight compounds. This synthesis strategy is directed to produce nanostructured ceramic components upon thermal conversion during which *in-situ* controlled growth of a nano-phase (metal or ceramic) occurs in the ceramic matrix.[55-59] Beside this, passive or active fillers can be also introduce in the polymer to form, after the pyrolysis, secondary phases in the polymer-derived matrix.[45a] The PDCs route has been widely applied to the preparation of h-BN in various geometric shapes. This is developed below. It should be mentioned that we deliberately focused on the use of two types of molecular precursors: borazine ($B_3N_3H_6$) and 2,4,6-trichloroborazine (also known as B-tricholoroborazine or simply trichloroborazine) ($B_3N_3H_3Cl_3$) denoted in this paper BZ and TCBZ, respectively (Fig. 2).

C Borazine and 2,4,6-trichloroborazine-derived h-BN

The extension of the molecular strategy to h-BN depicted in Fig. 1 is a synthetically challenge because the precursor is ideally expected to be composed of the pre-existing boron-nitrogen bonds and the hexagonal symmetry. Borazine-based precursors appear to be the most appropriate candidates because they are based on a six-membered ring structure of alternating boron and nitrogen atoms similar to h-BN. BZ and one of its derivative TCBZ are well known as useful precursors of h-BN.

BZ has been originally discovered by Alfred Stock in 1926.[60] It is a colorless liquid under standard conditions and offers the advantage to be volatile at low temperature (less than 60 °C under ambient pressure). BZ is considered to be planar and to have D_{3h} symmetry.[61] It has π-electrons and it shows weak aromaticity (although simple valence bond hybridization models predicted a planar structure and suggested possible multiple bonding (thus aromaticity) in the borazine ring) due to a strong pπ-pπ interactions between boron and nitrogen. The B-N bond distance in the borazine ring is 1.435 ± 0.002 Å. Hurwitz *et al.* found it to be economically competitive and attractive from a technical point of view.[62] Indeed, Wideman *et al.* reported in 1995 the possibility to prepare BZ by the reaction of cheap compounds such as $(NH_4)_2SO_4$ and $(NaBH_4)$ in tetraglyme at 120–140°C.[63]

TCBZ is a white solid compound more stable than BZ and can sublime above 60 °C.[64] However, TCBZ is corrosive when exposed to humid air because it can hydrolyse and release HCl. As BZ, it has to be therefore best stored at low temperatures and handled under an inert atmosphere. According to the presence of Cl atoms, TCBZ offers more possibilities to design preceramic polymers containing various nitrogen and carbon contents through reactions with linking reagent of the type of ammonia, amines or disilazanes. However, its synthesis is more complex and costly than the synthesis of borazine. The bottom-up approach uses borazine-based precursors with precisely controlled and tunable chemical composition that thermally decompose through a one-step strategy in vapour phase or through a multi-step process in liquid/solid phase into h-BN with different geometric shapes. Taking BZ as example of producing h-BN, vapor phase methods include thermal chemical vapor deposition processes (CVD)[65-66], ultra-high vacuum CVD (UHVCVD)[67-75], low pressure CVD (LPCVD)[76], plasma-enhanced chemical vapor deposition (PE-CVD)[77,78], spray-pyrolysis[32a], for example. Liquid/solid phase methods comprise thermolysis of BZ in autoclave-based processes to generate polyborazylenes (= preceramic polymers, PBZE) then pyrolysis to convert the polymers into h-BN.[34,37-41] In summary, BZ and TCBZ are very interesting compounds because they can be used both in vapor phase synthesis process and in liquid/solid phase methods. This is described in the following sections.

A h-BN by vapor phase synthesis from borazine (BZ) and 2,4,6-trichloroborazine (TCBZ). BZ and TCBZ have been both used in vapor phase synthesis processes to produce various types of geometric shapes (Fig. 2).

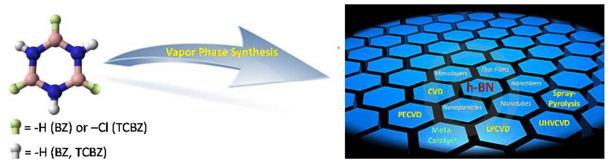

Figure 2. BZ and TCBZ–derived h-BN through vapor phase synthesis processes.

BZ is an ideal precursor for CVD-based processes as illustrated above. Within one step, this compound leads to the formation of nanoparticles, nanofibers, nanotubes and especially thin films and monolayers. By the hot-filament CVD (HFCVD) technique, quasi-spherical nanoparticles with sizes ranging between 20 and 50 nm and nanofibers with a length from 80 to 500 nm were generated.[79] Lourie *et al.* demonstrated the successful growth of BN nanotubes with the parallel-fringe patterns characteristic of multiwalled BN nanotubes (with length of ~5 µm and diameters of ~50 nm) from nickel boride particulate catalysts heated at 1000-1100°C using *in-situ* generated BZ.[80] This paper showed that CVD is usually combined with catalysts. Sneddon *et al.* reported the growth of double-walled BN nanotubes by a floating nickelocene catalyst CVD process from BZ at 1200 °C in a mixture of ammonia and nitrogen.[81] Depending on the BZ pressure, h-BN nanostructures could be either nanotubes (lower pressures, Fig. 3) or nanofibers (higher pressure). More recently, they compared the effect of the chemical structure of the h-BN precursors (BZ, decaborane) on the production of 1D h-BN nanostructures.[82] However, h-BN represents an ideal coating material against oxidation at high temperatures owing to its high thermal and chemical stabilities. Within this context, BZ is mainly used in vapour phase synthesis to produce thin films. In the 90th, Nagashima *et al.* published a series of reports on the epitaxial growth of single-crystalline BN films by thermal decomposition of BZ at 800 °C according to the equation $B_3N_3H_6$ + M (Ni, Pd, Pt) $\rightarrow$ h-BN/M (Ni, Pd, Pt) + $3H_2$ on different type of metallic substrates (Ni(111), Pd(111), Pt(111)).[67-70] Later, Auwärter *et al.* studied such monolayer h-BN films by X-ray photoelectron diffraction and scanning tunneling microscopy.[83,84] In 2004, Corso *et al.* reported the preparation of highly regular h-BN mesh films with a 3 nm periodicity and a 2 nm hole size by exposure of a Rh(111) single crystalline surface kept at 1070 °C to BZ vapors.[72,85] Since this report, the nucleation and growth reactions of h-BN on transition metal surfaces from BZ gained new interest.

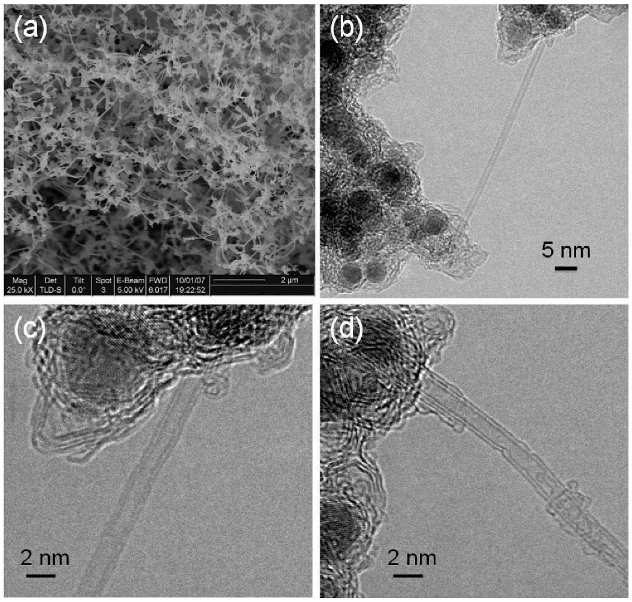

Figure 3. (a) SEM image, (b) low- and (c, d) HR TEM images taken from the double-walled h-BN nanotubes produced via floating catalytic CVD at lower BZ pressures.**[Reproduced with Permission from ref. 81]**

The growth of h-BN was investigated on different types of transition metals such as Pd[71,86], polycristalline Ni film or foil,[87] Ni(110)[88]/(111)[89,90], Ru(0001)[91], Pt(111)[92], Mo(110)[93] and Cr(110)[94]. Paffett *et al.* were the first to report the thermal decomposition of BZ on Pt(111) and Ru(0011) surfaces below 1000 °C.[95] The strong interest of BZ as a film precursor was also proved on other substrates such as Si(100) and SiBCN fibers with no decrease in their mechanical strength.[96] Recently, the structure of epitaxially grown h-BN on Ir(111) was investigated by CVD using BZ.[97] By photoelectron diffraction spectroscopy, authors demonstrated that a single-domain h-BN monolayer can be synthesized by a cyclic dose of BZ onto a metal substrate at room temperature followed by annealing at T = 1000 °C. Structural models for the h-BN monolayer on the Ir(111) surface were proposed.

TCBZ was considerably less investigated for vapor phase synthesis of h-BN than BZ most probably because of the complexity of its synthesis and the presence of chlorine atoms that implies the evolution of HCl concomitantly with the formation of BN. TCBZ is in general prepared according to the method of Brown and Laubengayer using BCl_3 as boron source and NH_4Cl as nitrogen source, which is not experimentaly trivial.[98] This precursor was used for h-BN CVD by Singh[99] and Gebhardt[100]. In particular, LPCVD technique was developed to deposit thin BN films. The LPCVD technique, deposition kinetics, and some of the physical characteristics of the deposited films were described by Singh[99] but Stolle and Wahl provided a more detailed investigation of the kinectic data for the CVD process of TCBZ to form stoichiometric BN layers on silicon substrates and on Tyranno® SiC fibers.[101] In this study, the decomposition of TCBZ was performed at temperatures between 700 and 960 °C according to the reaction $B_3N_3H_3Cl_3 \rightarrow$ 3BN + 3HCl. More recently, TCBZ was used to deposit h-BN by CVD at atmospheric pressure at 1000 °C on silicon carbide fibers.[102] It was demonstrated that the BN interphase allowed adjusting the fiber/matrix interface, thus causing a dramatic increase in the mechanical properties of the composites. Later, single-layer stoichiometric h-BN films were grown on Ni(111) at around 730 °C (Fig. 4).[103]

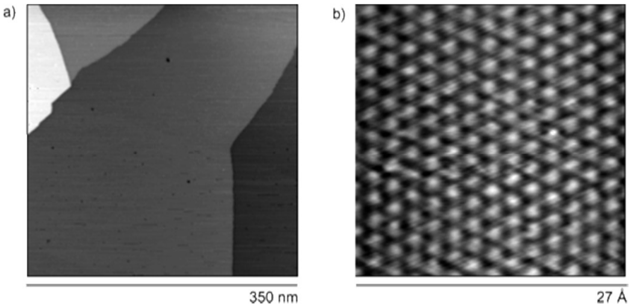

Figure 4. STM image from h-BN on Ni(111) as formed from B-trichloroborazine: (a) large scale image where large individual (111) terraces are seen (V_{sample} = −0.2 V, I_t = 1 nA); (b) atomic resolution zoom in (V_{sample} = −0.2 V, I_t = 30 nA, filtered). **[Reproduced with Permission from ref. 103]**

In 2005, Müller *et al.* reported the growth of h-BN on Pt(111) from TCBZ.[104] This led to the formation of domain structure, which had not been observed for systems with a very small lattice mismatch like h-BN/Ni(111). This paper clearly demonstrated that a change in precursor (TCBZ instead of BZ) significantly influences the resulting superstructures on the metal surface.

B h-BN from borazine (BZ) and 2,4,6-trichloroborazine (TCBZ)-derived polymeric precursor. BZ and TCBZ can be used as molecular precursors for the preparation of polymers such as polyborazylene (PBZE) and poly[B-aminoborazine] (PABZ), respectively. Direct polymerization of BZ occurs in a one-step process whereas the polymerization of TCBZ is performed via one or two steps, both approaches involving the nucleophilic substitution of chlorine atoms by linking groups before the polymerization itself. After polymerization, a pyrolysis step allows converting the PBZ/PABZ into h-BN powders (Fig. 5). The pyrolysis process is relatively complex and usually involves four steps: crosslinking, mineralization, ceramization and crystallization. By applying a conventional shaping process such as extrusion, casting, impregnation or pressing between the polymerization and pyrolysis steps, h-BN with particular shapes from 1D to 3D can be generated as illustrated in Fig. 5.

BZ is polymerized into a preceramic polymer, *i.e.*, polyborazylene (PBZ), by self-condensation at low temperature (Fig. 5). Thermolysis is achieved inside an autoclave to prevent volatilization of BZ during the process. According to the temperature, time and atmosphere (vacuum, argon, nitrogen), PBZ may be generated with approximate controlled molecular weights, tailored crosslinking degrees and various hydrogen, boron and nitrogen contents. Self-condensation of BZ was investigated in a large number of studies and the polymerization mechanisms have been identified.[34,37-41,105-114]

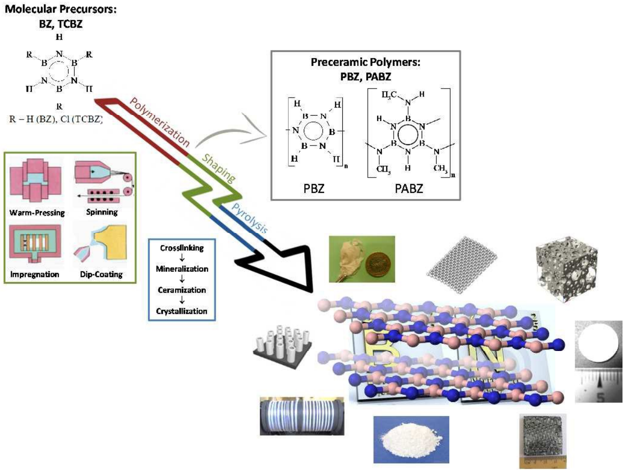

Figure 5. h-BN produced in the liquid/solid state from BZ and TCBZ.

It was demonstrated that self-condensation of BZ generated biphenylic and naphtalenic-type structures as illustrated in Figure 6 through condensation reactions of BH and NH units as well as probable ring-opening mechanisms in the PBZ.[105-108]

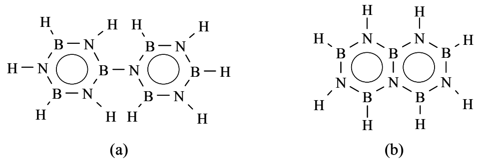

Figure 6. (a) Biphenyl and (b) naphtalenic-type units identified in PBZ through the self-condensation of BZ.

In the nineties, Sneddon *et al.* isolated a soluble branched-chain or partially cross-linked structure of PBZ by self-condensation of BZ under vacuum at 70 °C for ~48 h.[109-111] PBZ was then heat-treated in the temperature range 900-1450 °C under argon or ammonia leading to BN with high yield (84-93 %). Although the structure of the final material was turbostratic (with a low alignment of the basal planes of B_3N_3 hexagons), this is considered to be the first example of obtaining h-BN from PBZ. By the mean of spin coating of a glyme solution of this solid PBZ, Sneddon *et al.* reported for the first time in 1996 the preparation of BN films on a silicon substrate.[115] After pyrolysis up to 900°C in vacuo, uniform BN films of around 1000 Å were produced. In 2004, Interrante *et al.* used the same BN precursor solution to make SiC-BN composites, with allylhydridopolycarbosilane (AHPCS) as precursor of SiC.[116]The immiscibility of the two polymers leads to two-phase ceramic with increase in toughness after annealing up to 1600°CSeveral authors and in particular our group investigated also the structure of PBZ as well as the shaping potentialities of PBZ to produce h-BN geometric shapes. As an illustration, in 1993, Economy *et al.* reported the preparation of C/BN composites from PBZ.[112] In this paper, authors synthesized a viscous PBZ ($B_{3.0}N_{3.6}H_{3.7}$) by self-condensation of BZ at 70 °C for 40 h in an autoclave in a nitrogen atmosphere. Through the modification of the thermolysis rate of BZ to maintain certain mobility in as-formed molecules, similar to the mesophases already identified in pich (carbon precursor), authors demonstrated that they were able to obtain optically anisotropic phases during the thermolysis of BZ.[113] The idea behind this process was to improve the crystallinity of materials obtained from PBZ through the formation of an inorganic mesophase. This was demonstrated because the formation of the liquid-crystalline phase during thermolysis of BZ allowed producing materials with a high degree of crystallinity by heating up to 1800 °C. In 2001, Babonneau *et al.* investigated the structure of PBZ by means of ^{15}N and ^{11}B solid-state NMR.[114] Authors identified the presence of two types of boron environments including $\mathit{B}HN_2$ and $\mathit{B}N_3$ as well as two types of nitrogen environments ($\mathit{N}HB_2$ and $\mathit{N}B_3$). Furthermore and for the first time, eight-members B-N rings have been identified in PBZ.

In our group, we investigated the self-condensation of BZ in an autoclave at low temperature (45–60 °C) under argon to provide PBZ in various physical states and controlled crosslinking degrees (Fig. 7). The objective was to extend the possibilities to shape h-BN.[34,37-41]

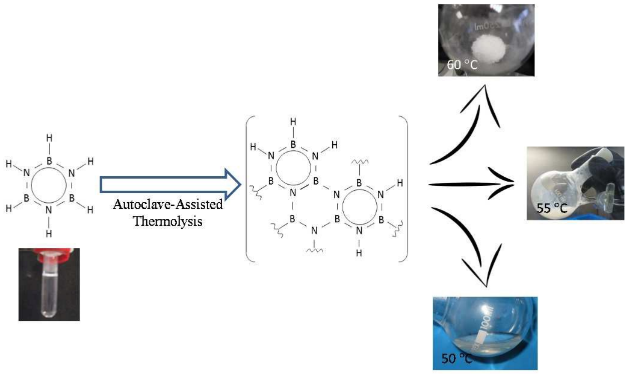

Figure 7. Polymerization of BZ into PBZ with different properties according to the thermolysis temperature.

As an illustration, PBZ prepared at 45-50°C is liquid (Fig. 7) and can be used pure or in solution in polar solvents as an interesting source of BN for shaping in solution such as dip-coating and infiltration of template or preforms. Liquid PBZ could be dip-coated on metallic (titanium, aluminum and copper) substrates to form protective BN coatings on metallic substrates after pyrolysis by infrared irradiation.[39] Volatilization of a part of the polymer occurred during the pyrolysis leading to a very thin coating with an uncontrollable thickness. The X-ray diffraction confirmed the formation of a poorly crystallized BN which rendered the coating air- and moisture-sensitive. Template-assisted PBZ (pure – liquid - or in solution) pyrolysis appeared also appropriate to access to the design of different morphologies of h-BN by (i) replicating the structure of a template material (mold) through the impregnation of the pore template with PBZ; (ii) performing the subsequent pyrolysis then (iii) removing the mold. Several examples can be described. Sneddon *et al.* reported the synthesis of free-standing BN nanoparticles as negative replicas of diatom frustules.[117] The starting frustule templates were impregnated by a glyme solution of PBZ,[109-111] followed by a pyrolysis at 1250°C and the dissolution of the siliceous frustule template. BN nanoparticles with micro- and nano- features inherited from the starting templates have been obtained in this seminal study. In another study,The filling of the straight cylindrical pores of a nanoporous anodic aluminum oxide (AAO) membrane (pore size = 200 nm) with a solution of liquid PBZ allowed generating arrays of mono-dispersed nanotubes after pyrolysis at 1200 °C to fully convert the polymer into ceramics.[38] During pyrolysis, the core of the PBZ nanowires was decomposed according to the fact that gas released and evaporation of low molecular weight species occurred during pyrolysis while a thin film remained and covered the pore walls as a result of the high surface energy of the alumina mould. BN nanotube arrays were generated after membrane dissolution. They displayed a turbostratic structure which crystallized by further heat-treatment above 1200 °C under nitrogen. Using the same replication strategy, porous materials can be prepared. BN foams were synthesized from liquid PBZ dissolved in THF to impregnate carbonaceous template foams.[37] After a pyrolysis at 1200°C under nitrogen and heat-treatment under ammonia at 1000 °C overnight to remove the template, foams with high porosity (~75 vol%), a specific surface area up to 300 $m^2.g^{-1}$ have been generated. An increase of the pyrolysis temperature to 1450 °C allowed improving the crystallinity of the material. Interestingly, the monolith-type foams displayed a hierarchical porosity with open-cell interconnected macroporosity (Fig. 8).

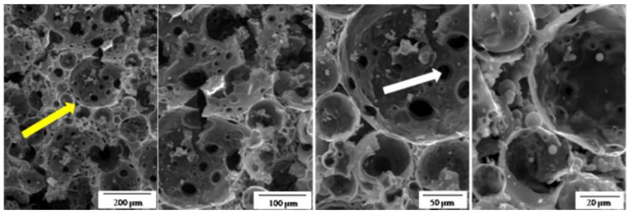

Figure 8. SEM micrographs of PBZ-derived foams obtained after pyrolysis to 1200 °C under nitrogen and heat-treatment under ammonia at 1000 °C overnight. The white arrows indicate the cells' internal junctions whereas the yellow arrows show the cells' external junctions. **[Reproduced from Ref. 37 with permission from The Royal Society of Chemistry]**

The unique combination of these properties of the proposed porous structure, *i.e.*, low density, high geometric surface area, permeability, tortuosity of flow paths and dimensional stability associated with the intrinsic properties of BN makes this class of porous architectures promising for specific functional purposes of significant interest such as filtration membranes, catalyst carriers, and even scaffolds for bone replacement. Using this strategy, we can tailor the porosity and specific surface area of h-BN. When synthesized in the solid state (60 °C), PBZ displays solubility at a suitable level to generate porous materials by replication. The interest is that solid PBZ displays a higher ceramic yields (90.9 %) than liquid PBZ (<55 %); therefore, a maximum of matter remains confined in the porosity of templates. This ensures a better control of the porosity by replication. Solution of solid PBZ could infiltrate a zeolite-templated carbonaceous replica.[40] Samples present a bimodal pore size distribution with a high proportion of micropores (≈ 0.20 $cm^3.g^{-1}$), a high specific area (568 $m^2.g^{-1}$) and a high pore volume (0.78 $cm^3.g^{-1}$). Solid PBZ appeared also adapted to plastic-forming techniques such as warm-pressing under 74 MPa at 60 °C to prepare highly dense (relative density of 86.3 %) monolithic samples after pressureless pyrolysis at 1450 °C under nitrogen in forms of disks.[34] Further annealing to 1800 °C induced relative density increase (93 %) and crystallization. To prevent the inherent brittleness of h-BN monoliths, we focused on the preparation of carbon fibers-reinforced h-BN matrix composites. They were manufactured using PBZ after 10 Polymer Infiltration Pyrolysis (PIP) cycles from solid one (5 first PIP cycles) and liquid one (5 last PIP cycles) and dissolved in THF.[41] The first PIP cycles were performed from solid PBZ because of its solubility in THF leading to solutions with adapted viscosity to infiltrate fibers preforms ensuring a high BN ceramic yield. However, the viscosity of the diluted solution of solid PBZ was too high after five PIP cycles to further infiltrate the fibers preforms. Therefore, we used diluted solutions of liquid PBZ which displayed a lower viscosity for the next five cycles. After each infiltration, the curing and pyrolysis processes are achieved at 85 °C and 1450 °C, respectively. C/BN composites exhibited a relative density of 94.7 % and an open porosity as low as 5.1 vol%.

The different examples described above have highlighted the high potential of PBZ to prepare various geometric shapes of h-BN using solution-based shaping process (infiltration, dip-coating) or plastic-forming techniques (warm-pressing) followed by pyrolysis. Based on the results reviewed previously, we can suggest that PBZ and therefore BZ are the most appropriate candidates to prepare h-BN at relatively low temperature (1450 °C) in an inert atmosphere *via* a "chemical route". However, the first disadvantage of this approach using BZ as molecular precursor is the crystallinity of the final material. The structure is turbostratic which may alter the thermostructural properties of materials produced from BZ. As a second disadvantage, the presence of reactive BH and NH units drastically limits the melt-processability of PBZ rather favouring the cross-linking reactions. As a consequence, the production of fibers by melt-spinning of PBZ is not possible without chemical modification of the polymers for limiting the crosslinking reactions thus improving the processing properties. Therefore, Sneddon *et al.* developed dipentylamine-modified polyborazylene as second-generation precursors to boron nitride, particularly as fibers.[118] The dipentylamine pendents were demonstrated to decrease the glass transition temperature (Tg) below the cross-linking temperature making these modified polymers good candidates for melt-spinning. Indeed, 30 μm diameter BN fibers smooth and uniform could be fabricated.

Concerning the first identified disadvantage, adding elements belonging to the alkali metal group at molecular scale in BZ or PBZ may be a way to significantly improve the crystallinity of the derived materials. This work is under investigation and will be published separately. Concerning the second disadvantage, the use of TCBZ to generate melt-spinnable polymers represents a solution, mainly because of the presence of chlorine atoms that offer the opportunity to react with linking reagents such as ammonia or amine. TCBZ-derived polymers, *i.e.*, PABZ, are described below.

TCBZ is likely the ideal molecular precursor for the preparation of processable polymers and the subsequent conversion into h-BN with the shape which has been imposed at polymer state. Two chemical approaches, which involve nucleophilic reactions of the chlorine atoms attached to boron with linking reagents, are reported in the literature to generate PABZ.

In a first strategy (two-step synthesis procedure), TCBZ reacts with ammonia or amine derivatives as linking reagents to form 2,4,6-(triamino)borazines (B-aminoborazines) which are subsequently thermolyzed at moderate temperature to generate PABZ. Pioneering works in this chemistry have demonstrated the preparation of B-(amino)borazine-type polymers through a two-step procedure[119-121], without focusing on their use as h-BN precursor. In the seventies, Tanigushi *et al.* have reported for the first time the preparation of h-BN fibers from a melt-spinnable PABZ prepared by reacting TCBZ with diethylamine to form an intermediate monomer. The subsequent ammonia treatment generated the PABZ.[122] Using methylamine as linking reagent to react with TCBZ followed by self-condensation of the as-obtained B-(trimethylamino)borazine above 200 °C in a nitrogen atmosphere, Kimura *et al.*[123] reported the synthesis of PABZ. The polymer is called poly[B-(trimethylamino)borazine] (Fig. 9).

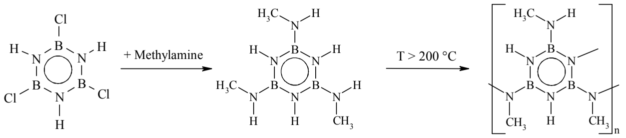

Figure 9. Reaction of TCBZ with methylamine followed by thermolysis to generate poly[B-(trimethylamino)borazine].

With addition of laurylamine as a blocking agent[123b], the cross-linking progress of the polymer during the thermolysis step was limited leading to the development of its melt-spinnability. Curing in air following by pyrolysis in ammonia and nitrogen atmospheres generated h-BN fibers with suitable mechanical properties (Tensile strength, σ = 0.98 GPa; Young's modulus, E = 78 GPa). Extending this work, our group investigated the evolution of the structure of poly[B-(trimethylamino)borazine] during the thermolysis of B-(trimethylamino)borazine (synthesized by reaction between TCBZ and methylamine) without blocking agents.[124] A series of different poly[B-(trimethylamino)borazine] could be generated by self-condensation of the B-(trimethylamino)borazine according to the selection of the thermolysis temperature from 140 to 200 °C.[125] Based on ^{15}N solid-state NMR and GC/MS experiments, we suggested that the structure of a typical melt-spinnable poly[B-(trimethylamino)borazine] ($[B_{3.0}N_{4.6}C_{2.1}H_{9.5}]_n$, $T_{thermolysis}$ = 180 °C) is composed of borazine rings, which are connected *via* a majority of -N(CH_3)- bridges resulting from loss of methylamine and a small proportion of NB_3-containing motifs (B-N bonds, biphenyl-type motif (Fig. 6a)) forming a three-dimensional network capped by a low proportion of peripheral -N(H)CH_3 groups. Bridging units was initially suggested by Lappert *et al.*[119] for the preparation of polymers in which borazine rings are linked by amino groups -N(R)- whereas NB_3-containing motifs, *i.e.*, extra-ring B-N bonds, was initially proposed by Gerrard *et al.*[120] and have been demonstrated by Paciorek *et al.*[126] Both the ratio between -N(CH_3)- bridges and B-N bonds and the relative amounts of -N(H)CH_3 groups caused different responses to thermal properties and spinnability (glass transition, spinning temperatures, melt throughput, and fiber drawing). -N(CH_3)-bridges provide flexibility, while -N(H)CH_3 end groups act as plasticizers upon heating at moderate temperature. In contrast, NB_3-containing motifs contribute to the rigidity of the polymeric network. The proportion of bridging units and -N(H)CH_3 end groups is significant below 160 °C which explains the lack of stability of the polymer fiber during extrusion and stretching (Fig. 10a).

Their proportion decreased upon heating to the benefit of NB_3-containing motifs (=extra-ring B-N bonds). As a consequence, melt-spinnability was improved above 160 °C but decreased in the temperature range 185-200 °C according to the presence of an important portion of NB_3-containing motifs (Fig. 10b and c, respectively).[125] As a consequence, a compromise needs to be found and it was demonstrated that melt-spinnable compounds were prepared between 160 and 185 °C. Such polymers displayed a chemical formula of $[B_{3.0}N_{4.4\pm0.1}C_{2.0\pm0.1}H_{9.3\pm0.2}]_n$ (n ∼ 7.5), a glass transition between 64 and 83 °C, tailored flexibility, and sufficient plasticity to successfully produce fine-diameter green fibers, then h-BN fibers by curing and pyrolysis.

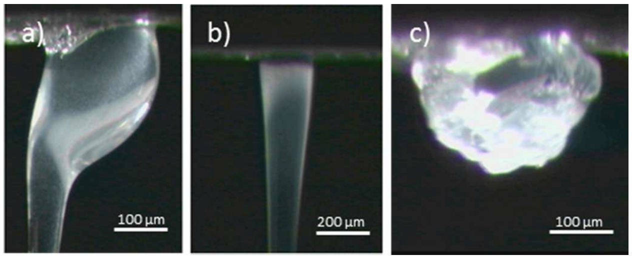

Figure 10. Behavior of the poly[B-(trimethylamino)borazines] during extrusion: 140 °C (a), 165 °C (b) and 195 °C (c).

Selecting special amines instead of (mono)methylamine provides one opportunity of major importance, since through the functionality of the amine, primary or secondary, the degree of cross-linking, and thus the viscosity and the ceramic yield of the resulting polymer, can be tuned. Following this methodology, our group has developed a route through the two-step nucleophilic reaction of TCBZ with various amine derivatives yielding molecular compounds **1-3** (Fig. 11)[127] Comparison was made with the symmetric B-(trimethylamino)borazine **4** (Fig. 11)[125] which provide melt-spinnable polymers as described above.

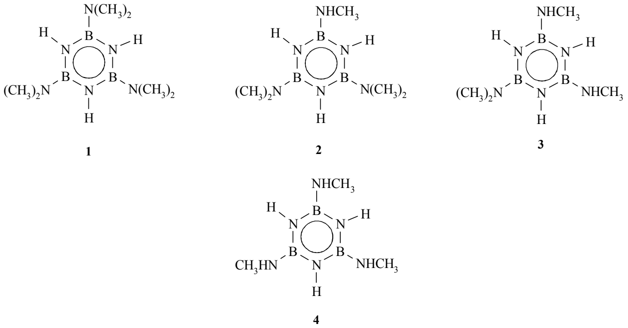

Figure 11. Structure of assymetric B-(alkylamino)borazines (**1-3**) and comparison with the B-trimethylaminoborazine (**4**).

The self-condensation of every B-(alkylamino)borazine in an argon atmosphere allowed the establishment of bridging units as well as direct extra-ring B-N bonds yielding the related poly[B-(alkylamino)borazine], thus revealing competition between the different reaction mechanisms confirmed in ref. 125. The proportion of bridging units is seen to decrease going from **4**- to **1**-derived polymers. It was confirmed that the presence of bridge-type bonds in such poly[B-(alkylamino)borazine] provides flexibility and an increased melt-spinnability, thus leading to the conclusion that melt-spinnability increased from **1**- to **4**-derived PABZ. In addition, the ceramic yield is reduced with an important proportion of $N(CH_3)_2$ in the B-(alkylamino)borazine leading to important shrinkages during the further polymer-to-ceramic conversion of green fibers derived therefrom.[127] Hence, the **4**-derived PABZ presented the best interest to produce h-BN fibers with high performances (Fig. 12).[128]

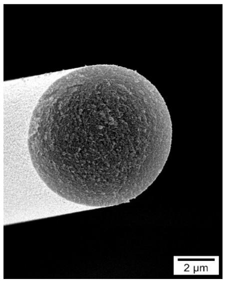

Figure 12. Typical morphology of Poly[B-(trimethylamino)borazine]-derived h-BN fibers.

In a second strategy to prepared TCBZ-derived PABZ, TCBZ reacts with linking reagents such as silazanes in a one-step synthesis procedure. The earliest successful efforts to prepare PABZ according to this one-step synthesis procedure have been carried out by Paine *et al.*[129] They have synthesized a large variety of polymers by reaction of TCBZ with disilazane derivatives. Starting from TCBZ, highly 3D cross-linked gels have been obtained by reaction with hexamethyldisilazane (HMDS) (Fig. 13).

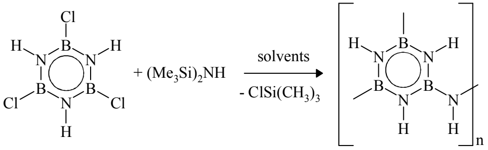

Figure 13. Reaction of TCBZ with HMDS.

Thermolysis mechanisms through bridging unit (-N(H)-, -N(CH_3)-) formation has been demonstrated. N(H)Si(CH_3)$_3$ ending groups are shown to survive after thermolysis. Pyrolysis of polymer at 900 °C under vacuum, then briefly to 1200 °C in air results in the formation of h-BN. Using an alternative pyrolysis procedure in an ammonia atmosphere to 1200 °C, then 1600 °C in a nitrogen atmosphere, highly crystallized h-BN was generated. Building-up these results through the preparation of highly microporous h-BN[130] and thin coating[131], they have devoted their study to the synthesis of linear PABZ using a blocking group attached to one boron atom in TCBZ, forming N-dimethyl B-dichloroborazine.[132] These insoluble gels are interesting candidates for the preparation of h-BN powders after pyrolysis at 1200 °C in ammonia and nitrogen atmospheres. Oxidation resistance of these ceramics is good at temperature as high as 900 °C. A similar approach has been reported by Paciorek *et al.* who have prepared PABZ through nucleophilic reactions on the boron atoms bearing the chlorine atoms in TCBZ.[133,134] The as-synthesized polymer is soluble in pentane and hexane but does not melt upon heating preventing the preparation of complex shapes by melt-processing such as melt-spinning. However, its good solubility makes it a good candidate for the preparation of h-BN matrices and coatings for ceramic fibers through pyrolysis at 1000 °C in an ammonia atmosphere. A significant improvement of the oxidation resistance of carbon fibers was observed with the h-BN matrices. Based on these selected examples, it is clear that TCBZ is an appropriate molecular precursor to generate melt-processable polymers whereas PBZ must be modified. However, the two main disadvantages of PABZ are (*i*) their weight loss occurring during the pyrolysis under ammonia to 1000 °C (generally in the range 45 – 55 %) and (*ii*) the necessity to increase the final temperature to 1800 °C to obtain h-BN with a sufficient degree of crystallinity. Using BZ, it is possible to generate PBZ with significantly higher ceramic yield (> 90 %). Furthermore, reactive gases are not required during the pyrolysis according to the absence of carbon-based groups in PBZ. This highlights that combining all the properties required for preparing h-BN in various geometric shapes, *i.e.*, sufficient cross-linking, solubility, fusibility, high ceramic yield, in only one molecule (or macromolecule) is extremely ambitious and generally not possible.

Conclusions

h-BN is the focus of important research since its discovery in the early 19th century mainly. It can be prepared according to various approaches. This review stated the development in the preparation of h-BN by bottom-up approaches using borazine-based molecular precursors. Borazine and 2,4,6-trichloroborazine are appropriate h-BN precursors according to the fact that they display the six-membered ring structure of alternating boron and nitrogen atoms found in h-BN. They can be decomposed within a one-step strategy in vapor phase using mainly CVD-based methods to form nanomaterials and thin films. According to the presence of reactive sites in their structures (BH, NH, BCl), borazine and 2,4,6-trichloroborazine can also yield polymers of the type polyborazylene and poly[B-(amino)borazine] respectively by thermolysis and/or reaction with a linking reagent such as ammonia or amine. The condensation degree of as-obtained polymers can be controlled to be adapted to a large variety of shaping process (usually used for organic polymers). The subsequent pyrolysis allows their conversion into h-BN with various geometric shapes such as (nano)fibers, films, monoliths and some of them can be prepared with a controlled porosity and a hierarchical porosity. The materials based on precursor-derived h-BN have a great potentiality which shows that the relatively recent Precursor Derived Ceramics (PDCs) route is a promising technology for different challenging applications in the future. In fact, up to now, the applications of these precursor-derived h-BN materials are extremely limited. However, taking into account that ceramics will have increasing applications in environmental and green technologies, also the materials based on precursor derived h-BN should be further developed in these fields, especially by the combination of h-BN with low molecular weight compounds to form multifunctional materials after pyrolysis that combine the properties of h-BN with those of a second phase for the fields of energy conservation (e.g. hydrogen storage), environmental protection or fuel cells. Therefore much additional development work is necessary.

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