

Polycondensation of Urea and Boric Acid to give Polyborate Ester, A Precursor for Boron Nitride

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Abstract. Polycondensations (condensation polymerization) are stepwise reactions between bifunctional or polyfunctional components, with elimination of simple molecules such as water or alcohol and the formation of macromolecular substances. Polyborate ester, formed by this process, gives ceramic materials during pyrolysis. Polymer pyrolysis offers an attractive alternative to the typical high temperature powder processing approach in the fabrication of high-performance ceramics. This approach might also prove to be useful in the fabrication of fibers, coatings, and composites. It is within this framework that the present study was undertaken; its aim is the preparation of boron-containing oligomeric precursors which gives boron nitride after pyrolysis. The precursor was synthesized by the condensation reaction between boric acid and urea (or other N-containing reactive multifunctional compounds). The oligomeric precursor and its pyrolysed products were thoroughly characterized by elemental analysis, IR, NMR, XRD, Thermal Analysis and Transmission Electron Microscopy (TEM). The elemental analysis results of the oligomer are--- C-13.40%, H-5.97%, N-32.44% and B-17.09%. X-ray diffraction and TEM studies showed that boron nitride obtained from this system possess tetragonal structure.

Introduction

One commercially important non-oxide ceramic is boron nitride, BN. BN offers an inherent advantage over carbon in that it does not oxidize rapidly below 850°C. Like carbon, BN has a relatively high thermal conductivity but is an insulator with a low dielectric constant. This deceptively simple material has widespread use, particularly in a narrow range of thermal/ structural applications, but deficiencies in synthetic and processing methods have ultimately restricted its utilization in many advanced ceramic applications. Nonetheless, several renewed interest in its chemistry and processing, and demands have appeared for fibers, coatings, and foams that cannot be obtained by classical high-temperature powder preparation methods [1]. Pyrolysis of polymers for the synthesis of non-oxide ceramics has been investigated in recent years [1]. Synthesis of pure non-oxide ceramics, specially nitrides and borides, through a polymeric precursor route is still to be developed. A variety of boron-containing polymers have been investigated as ceramic precursor materials [1]. Pyrolysis of these polymers gives boron nitride (BN), boron carbide (B₄C), and boron oxide. Among these polymers, considerable attention has been recently focussed on polymers that can be used to synthesize BN. Most approaches to the synthesis of polymers whose pyrolysis results in BN involve the use of borazines as starting materials [2]. Seyferth and Coworkers [3] have developed new preceramic polymers, which are produced by the reaction of decaborane-14 with various diamines such as H₂NCH₂CH₂NH₂, Me₂NCH₂CH₂NMe₂, HN(CH₂CH₂)₂NH, and N(CH₂CH₂)₃N in diethyl ether. The polymers are converted to ceramic powders by pyrolysis in the temperature range from 1000 to 1500°C at a heating rate of 10°C/min in a stream of argon.

Sneddon and Coworkers [2] have been studying the production of several new boron polymers, poly(vinylborazine), poly(vinylpentaborane), and poly(borazylene), which are useful precursors of B-containing ceramics such as boron nitride and boron carbide in high yields. B-vinylborazine can be readily polymerized either thermally or with the aid of free radical initiators to produce a soluble new polymer, poly(B-vinylborazine) which gives h-BN during pyrolysis under an ammonia atmosphere. Recent work has demonstrated that boron nitride(BN) can be synthesized with a very high yield from polymeric precursors. But as starting materials, borazines and decaboranes are highly toxic, hazardous and expensive. So, the focus of our current research is to synthesize BN from oligomeric precursors through a simple, cost-effective, non-toxic route. In the present study we synthesized a B-containing oligomeric precursor from the reaction between boric acid and urea, which gives boron nitride and carbonitride during pyrolysis.

Experimental

Boric acid was obtained from SRL, India and purified by crystallizing three times from water, filtered and dried to constant weight over metaphoric acid in a desiccator. Urea was obtained from SRL, India, which was recrystallized twice from conductivity water. The crystals were dried under vacuum at 55°C for 6 hr [4].

The precursor was synthesized by refluxing the mixture of boric acid and urea in xylene / toluene for about 4hrs. The raw materials were taken in their respective stoichiometric ratio. By measuring the weight loss, the end point of the reaction was determined. Water evolved during the course of reaction was removed by using Dean & Stark apparatus. A white colored solid product was formed which was also known as polyborate ester. The product was recrystallized from ethanol. The oligomer was then pyrolysed in air at 400°C and 800°C for 3hr. Pyrolysis of the oligomer yields a grey powder at 400°C and a white powder at 1000°C respectively.

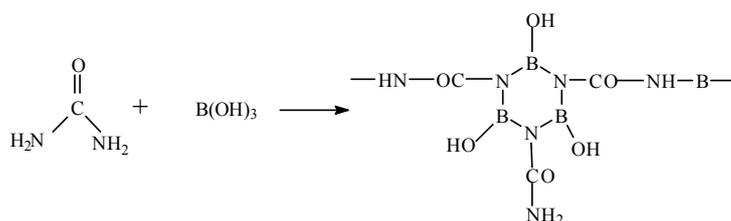
The IR spectra of the oligomer and its pyrolysed products were recorded using Shimadzu Infrared Spectrophotometer (IR-470). The ¹H and ¹³C NMR spectra were recorded by Bruker AC 200 spectrometer at a frequency of 200 MHz. DMSO-d₆ was used as solvent and tetramethylsilane (TMS) as internal standard. The ¹¹B NMR spectrum was taken in the solid state. CHN-analysis of oligomers was obtained from a 2400 Series II CHN Analyser, Perkin Elmer, USA, using helium as the driving gas and oxygen as the combustion gas. Boron analysis of the oligomer was obtained from Galbraith Laboratories, Inc., USA. Thermal analysis(DTA/TGA) of the oligomer was done by using Stanton Redcroft(STA 625) thermal analyzer in air with a heating rate of 10 deg/min. An X-ray diffraction study of the oligomer and its pyrolysed products was carried out with the aid of Philips PW-1729 X-ray diffractometer using a Co source.

Results and Discussion

Boric acid is known to react with urea to give a low molecular weight oligomeric precursor. Without giving any details, T.E. O'Connor [5] reported that boric acid reacts with urea to give a polymeric precursor, which subsequently gives boron nitride upon pyrolysis. In the present work an attempt has been made to synthesize and characterize the precursor oligomer and its pyrolyzed products obtained from the reaction between urea and boric acid thoroughly. Regarding the structure of the boric acid-urea condensation product (polyborate ester), the details have not been clarified yet. However, the following proposed structure is usually accepted.

The melting point of the polyborate ester is 160°C. The above mentioned precursor is soluble in ethanol, methanol, water, DMSO, Dioxan etc. but insoluble in CHCl₃, THF etc. The elemental analysis values (in wt.%) of the precursor are, C-13.40, H-5.97, N-32.44, B-17.09 which

match very well with the calculated values (in wt.%) C-13.48, H-2.62, N-31.46, B-16.48 based on the above proposed structure.



From the representative infrared spectra of the precursor and its pyrolyzed products at I) 400°C and II) 1000°C the frequencies (cm^{-1}) of the important peaks are assigned and tabulated below.

Table I. Assignment of Important Peaks for Urea-Boric acid Condensate and Its Pyrolyzed products

Major IR bands with frequencies(in cm^{-1})	Precursor	Pyrolyzed products at 400°C	Pyrolyzed products at 1000°C
N-H stretching	3305	3395	-
C=O stretching (amide I)	1650	1652	-
N-H deformation (amide II)	1590	-	-
B-N stretching	1420	1435	1445
B-N bending	784	782	772
C-N stretching	1348, 1230	1248	1249
B-O stretching	1080	1025	-

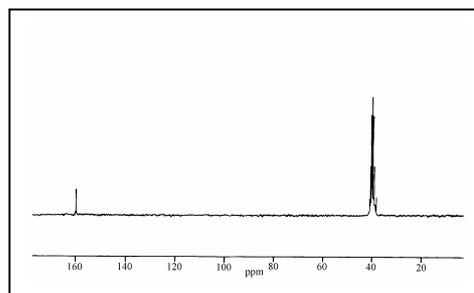
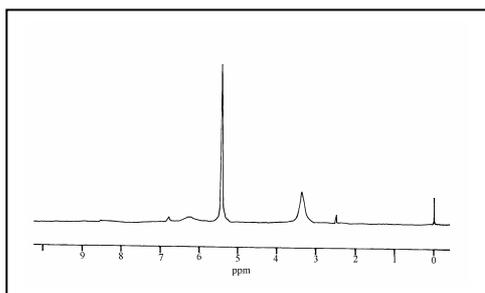


Fig.1 ^1H NMR spectrum of the Polyborate ester Fig.2 ^{13}C NMR spectrum of the Polyborate ester

^1H and ^{13}C NMR spectra of the precursor are shown in Figs. 1 and 2. In the ^1H spectrum the first peak at 2.5 ppm is due to DMSO- d_6 . The other peaks at 3.3, 5.4 and 6.2 ppm are due to the protons related to B-OH, CO-NH $_2$ and CO-NH groups respectively. In the ^{13}C spectrum a single peak (besides the solvent peak) at 159.684 ppm appears due to the amide carbon. In the ^{11}B solid state NMR spectrum of the precursor, a single resonance at 1.262 ppm is observed due to the same environment of boron in the precursor. From the IR and NMR spectra the above structure of the polyborate ester has been proposed.

The TGA/DTA experiment (Fig.3) showed two sharp and pronounced endothermic events at 131.21°C and at 165.65°C. The first endotherm was due to evolution of moisture from the hygroscopic oligomer and volatile matters like NH $_3$, CO $_2$ etc. This coincided with a sharp (TGA)

weight loss of about 40.41%. The second endotherm was due to the melting of the oligomer. Here no weight loss was observed. After that there was no weight loss.

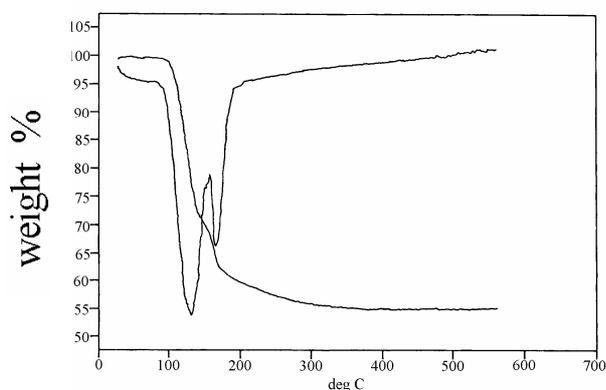


Fig.3 TGA/DTA curve of the polyborate ester

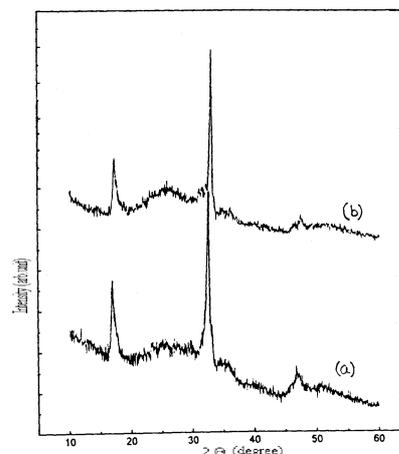


Fig.4. X-ray Diffraction pattern of the Pyrolysed Products of Oligomer (a) at 400°C and (b) at 1000°C.

From the X-ray diffraction pattern of the oligomer it is observed that the oligomer is highly crystalline in nature. XRD pattern of the pyrolyzed products of oligomer at a) 400°C and b) 1000°C are shown in Fig.4 Both XRD patterns show diffraction peaks at same diffraction angle. The presence of a diffraction peak at about $2\theta = 32.94^\circ$ with d-spacing value of 3.15(121) corresponds to boron nitride. The first X-ray diffraction peak at about $2\theta = 17^\circ$ with d-spacing value of 6.05\AA has been assigned to the compound CN_x after correlation with the IR data. Another X-ray diffraction peak is at about $2\theta = 47^\circ$ with d-spacing value of 2.24\AA has been specified to $\beta\text{-C}_3\text{N}_4$ [6].

Conclusion

Polyborate ester based on boric acid and urea has been synthesized and thoroughly characterized, which on pyrolysis yielded boron nitride and carbonitride. Ammonia gas, boron trichloride gas, and cyanide compounds that have been employed for the synthesis of boron nitride are not used in this process. During the course of study it is found that the boric acid ester with urea is stable to thermal treatment. The coexisting boron nitride and carbonitride formed by this process is considered to be a sort of unique composite ceramics.

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