Synthesis and Characterization of Processable Polyborate Precursors

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Abstract. Polyborates have been formed by disproportionation and polycondensation of trimethoxyboroxine and also of trimethoxyboroxine and boric acid. The critical role of stoichiometry in the formation of polyborates without requiring incorporation of a metal counter ion is revealed. The emphasis is on integration of this chemistry with fabrication processes. Incorporation of an appropriate linear organic polymer is shown to yield the required rheological and thermal characteristics in this regard. These polyborates are inferred to be suitable as precursors for boron nitride in geometrical forms that can be processed as supported structures. However, they are also determined to be unsuitable as precursors for boron nitride fibers, oriented or isotropic, primarily due to their low glass transition temperature.

Keywords: polyborate, sol-gel, ceramic precursor, boron nitride

1 Introduction

An infinite series of polyborates can be envisaged with increasing ratios of boron to alkoxyls and hydroxyls with their limiting structure being boron oxide. A polyborate is any dealkoxylated or dehydrated boron oxide precursor intermediate in the series from a boron alkoxide or boric acid to boron oxide, (RO)₃B ... (ROBO)₃ ... (ROBO)₆·B₂O₃ ... B₂O₃ where RO may be either alkoxyl or hydroxyl groups [1]. Trace amounts of alcohol will serve to solubilize the oxide and introduce both alkoxyl and hydroxyl groups into the B₂O₃ matrix. Polyborates have been prepared from cyclohexanol and boric acid or boron oxide by removing water azeotropically from a toluene or xylene solution or by direct reaction of boron oxide with cyclohexanol, producing boric acid as a by-product [1, 2]. Analogous reactions with boron oxide have also been performed with lower boiling alcohols, such as isopropyl alcohol. Polyborates are more thermally stable than the initial alkoxide or corresponding metaborates since they are closer to boron oxide, a highly thermally stable species. However, polyborates hydrolyze rapidly with exposure to water to give boric acid and the corresponding alcohol [1].

It has been demonstrated in our laboratories [3, 4] that lithium polyborate gels can be formed from trimethoxyboroxine and lithium methoxide in a hydrolytic environment. Fiber formation prior to gelation can be effected in polyborate systems with a lithium counterion. Microstructural examination of the lithium polyborate fiber samples by scanning electron microscopy showed a highly porous microstructure. The tendency to form the trimeric ring containing both tricoordinate and tetracoordinate boron atoms and the stability of the tetracoordinate boron with respect to hydrolysis are important aspects in the formation of polyborates by this route [5]. However, once an alkali metal counterion is incorporated into a polyborate structure it is very difficult, if not impossible, to remove it [4]. Hence, synthetic possibilities to generate polyborate structures directly without a counterion have been explored.

Concerns over the presence of residual organics, such as toluene or xylene which may lead to excessive
carbon during thermochemical conversion or, alternatively, the presence of metal ions that may be difficult to remove from polyborate precursors, have motivated the development of direct polycondensation of trimethoxyboroxine and boric acid to form a polyborate (Eq. 1) [6, 7]. It has been reported that disproportionation of trimethoxyboroxine above 130°C also leads to formation of a polyborate (Eq. 2) [1]. Since both condensation and disproportionation can occur simultaneously above 130°C, formation of a polyborate is shown in Eq. 3 with incomplete conversion of trimethoxyboroxine to boron oxide with both reactions implied.

\[
4(\text{CH}_3\text{OBO})_3 + \text{B(OH)}_3 \xrightarrow{>110\degree C} 3\text{B(OCH}_3)_3 + 3\text{CH}_3\text{OH} + 5\text{B}_2\text{O}_3 \quad (1)
\]

\[
(\text{CH}_3\text{OBO})_3 \xrightarrow{>130\degree C} \text{B(OCH}_3)_3 + \text{B}_2\text{O}_3 \quad (2)
\]

\[
\begin{align*}
\text{CH}_3\text{O} & \quad \text{B} \quad \text{O} \\
\text{B} & \quad \text{O} \quad \text{CH}_3 \\
\text{O} & \quad \text{B} \quad \text{O} \\
\text{O} & \quad \text{OH} \\
\text{O} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{OCH}_3 & \quad \text{B} \quad \text{O} \\
\text{B} & \quad \text{O} \quad \text{O} \\
\text{O} & \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{OH}, & \quad \text{B(OCH}_3)_3 \\
\text{100\degree C to 265\degree C} & \quad \text{CH}_3\text{OH}, \quad \text{B(OCH}_3)_3
\end{align*}
\]

\[
R = \text{H, CH}_3 \text{ or boroxine ring}
\]

The ability to process polyborates can be enhanced by the addition of a low concentration of a linear, high molecular weight polymer, such as poly(methyl methacrylate) which is soluble in trimethoxyboroxine. This is especially true when the composition is solution-based or the polyborate has been formed with only a low degree of conversion of the initial boron alkoxide. The idea of incorporating a high molecular weight polymer, that is fugitive during pyrolysis and leaves little or no carbon, is not new. Silazane precursors to silicon nitride have been spun with added poly(ethylene oxide) [8]. Poly(vinyl acetate) has been added to a partially hydrolyzed aluminum alkoxide precursor for Al$_2$O$_3$ fiber and also to a silicon alkoxide precursor for Al$_2$O$_3$-SiO$_2$ fiber in order to adjust the viscosity of the solutions for fiber drawing [9, 10].

The focus of the study reported here has been on integration of the synthetic chemistry of polyborates with the critical requirements for processing them. While processability of the polyborates was studied through fiber formation, much of what has been learned in this process is likely to be of greater relevance to coatings and films. The major barriers that exist in following this route for polyborate-based ceramic fibers are clearly revealed and discussed.

2 Experimental

2.1 Materials

Trimethoxyboroxine was obtained from Aldrich and Callery Chemical Companies. Poly(methyl methacrylate) was obtained from Rohm & Haas. It had a viscosity-average molecular weight of 135,000 g/mole. Gases used were prepurified grade nitrogen (99.998% minimum), dry grade air, and anhydrous grade ammonia (99.99% minimum) from Matheson Gas Products. Ultrahigh purity grade argon (99.999% minimum) was obtained from Holox. High temperature silicone bath oil was obtained from Ace Glass. Boric acid (99.99%), hexagonal boron nitride and all other chemicals were obtained from Aldrich Chemical Company.

2.2 Synthesis and Processing of Polyborates

A series of polyborates were made by varying the stoichiometry of trimethoxyboroxine (TMBO) and boric acid (BA). 1:1, 2:1, 3:1, 4:1, 6:1, 10:1, and 1:0 initial mole ratios of TMBO to BA were polymerized. Reactions typically were based on 200 ml of TMBO (1.378 moles). A 500 ml reaction flask with teflon boiling chips and a 250 ml receiving flask were used on a high boiling distillation apparatus (Ace Glass Model 6563). The reaction flask was immersed in a silicone oil bath. Boiling began in the flask as the TMBO-BA slurry was heated to 115°C under a slight vacuum (630 to 660 mm Hg). At this temperature, boric acid was observed to go slowly into solution. However, with TMBO alone, boiling began at approximately 130°C. A distillate, comprising of methanol and trimethyl borate, began to collect in the receiving flask at 5 to 10°C higher than the observed boiling temperatures.

The silicone oil bath temperature was increased gradually to maintain distillation. To obtain a high conversion of trimethoxyboroxine to polyborate, the reaction flask was heated to as high a temperature