Synthesis of Poly(borazinylamine)

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ABSTRACT: 1,3,5-Trichloroborazine (TCB) was prepared from the reaction of ammonia chloride with boron trichloride. TCB along with hexamethyldisilazane and boron trichloride were used to synthesize boron nitride (BN) preceramic polymer poly(borazinylamine). This study showed that, the lower the reaction temperature, the higher the synthetic yield. Poly(borazinylamine)'s solubility mainly depended on the ratio of TCB, $(Me_3Si)_2NH$, and BCl_3. The solvent used in the reaction had a large effect on the ceramic yield of poly(borazinylamine). A soluble poly(borazinylamine) with good synthesis and ceramic yields was obtained when the reaction temperature was −15°C, cyclohexane was the solvent, and the ratio of TCB : $(Me_3Si)_2NH$: BCl_3 was 1 : 6 : 1. By means of infrared and mass spectroscopy analyses, the structure of the poly(borazinylamine) was identified. Thermal decomposition of the poly(borazinylamine) precursor to hydrolyzed BN was also examined. Hydrolyzed BN was obtained at 1000°C, where the ceramic yield was 35–45%. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 863–868, 1999

Key words: boron nitride; precursor; poly(borazinylamine); synthesis

INTRODUCTION

Boron nitride (BN) is an advanced inorganic engineering ceramic material, and it has enjoyed widespread attention with the development of high technology.[1,2] Soluble and/or fusible preceramic polymers offer several unique benefits in the manufacture of complex, multifunctional materials. Polymeric precursors that convert to shape articles without complex processing would alleviate many processing problems and would be of great value. The potential stability and structure relationship between poly(borazinylamine) and BN has been described.[3] However, it was also pointed out that poly(borazinylamine) was insoluble, infusible, and essentially impossible to process probably as a result of significant crosslinking chemistry, even at relatively low temperature.[4] In the present study, BCl_3, NH_4Cl and $(Me_3Si)_2NH$ were used as raw materials to synthesize poly(borazinylamine). The effect of solvent, reaction temperature, and ratio of raw material on synthesis yield, solubility, molecule structure, and ceramic yield of poly(borazinylamine) was investigated in detail.

EXPERIMENTAL

Synthesis of 1,3,5-Trichloroborazine (TCB)

Dry NH_4Cl powder was mixed with active carbon in the relative mass ratio of 0.63 : 0.37. The mixture was placed in a quartz reactor and kept at 150°C. By aerating BCl_3 slowly into the reactor, 1,3,5–TCB acicular crystals were obtained at the other end of the reactor.

Synthesis of Poly(borazinylamine)

TCB and solvent were quantitatively added to a three-holed flask. The temperature of the reaction liquid was dropped to the point needed, while the liquid was being agitated. The reaction mixture

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Table I Synthesis Condition, Synthesis Yield, Properties, Solubility, and Ceramic Yield of Poly(borazinylamine)

	Synthesis Condition						
No.	Temperature (°C)	Solvent	TCB : $(Me_3Si)_2NH$: BCl_3	Product Properties	Solubility	α_1	α_2
1	0	Cyclohexane	6 : 5.5 : 0	White powder	Insoluble	5.4	42.67
2	0	Ether	5 : 26.3 : 4	Puffy lump, white resin	Soluble	6.4	31.79
3	0	Chlorobenzene	6.5 : 68.5 : 10.5	Translucent lump, white resin	Insoluble	4.5	44.37
4	−15	Cyclohexane	5 : 26.3 : 3.2	Sticky, white resin	Soluble	14.8	36.98
5	−15	Ether	5 : 52.7 : 11.5	Porous lump, white resin	Insoluble	9.7	30.14
6	−15	Chlorobenzene	5 : 4.8 : 0	White powder	Insoluble	18.4	46.25
7	−40	Cyclohexane	5 : 52.7 : 17.5	White resin	Dissoluble	16.0	40.26
8	−40	Ether	5 : 7 : 0	Light yellow resin	Insoluble	15.9	17.20
9	−40	Chlorobenzene	5 : 26.3 : 5	Translucent white resin	Insoluble	14.1	35.90

α_1, synthesis yield (%); α_2, ceramic yield (%). Synthesis yield is calculated by mass of obtained poly(borazinylamine) (g)/mass of boron element in reaction (g). Data in the "TCB : $(Me_3Si)_2NH$: BCl_3" board is proportioned by mass (g).

was aerated with BCl_3 quantitatively and slowly. Next, $(Me_3Si)_2NH$ was dripped into the flask for 2 h. After that, the reactants were kept at a low temperature for one more hour. The solvent and unreacted reactant were then removed by filter or vacuum distillation at room temperature, and poly (borazinylamine) was obtained in powder or resin form.

Characterization of Poly(borazinylamine)

Infrared spectra were recorded on a Hitachi 270-30 spectrometer in the 4000–400 cm^{-1} frequency range. Samples were studied as powder dispersed in a KBr pellet. To obtain detailed information about the decomposition processes of poly(borazinylamine), a differential thermal analyzer (DTA; CDR-1), a thermogravimetric (TG) analyzer (Rigaku-Thermoflex), and a mass spectrometer (KYKY-QP1000A) were used. Ceramic yields were determined by sintering poly(borazinylamine) at 1000°C in nitrogen.

RESULTS AND DISCUSSION

Factors That Affect the Synthesis of Poly(borazinylamine)

Orthogonal Experiment Result

The main factors affect the synthesis of poly(borazinylamine) are reaction temperature, solvent, and ratio of materials. If three different levels in each factor were constituted, experiments of 27 series should be conducted. Combinatorial optimization method of multifactors in the orthogonal design was adopted in the present study. Apply L_9 orthogonal array mechanically. Experimental conditions and results were shown in Table I.

Data Processing

The purpose of this investigation was to obtain poly(borazinylamine) with high synthetic yield, ceramic yield, and good processability. Thus, the solubility, synthetic yield, and ceramic yield of poly(borazinylamine) were used as criteria to evaluate the above three main factors comprehensively. Experimental results in the present investigation were processed quantitatively, as shown in Table II.

Effect of Raw Materials Ratio on the Solubility of Poly(borazinylamine)

From Figure 1, it is apparent that the factors that affect the solubility of poly(borazinylamine) are a ratio of raw materials, solvent, and temperature (in order of importance). Low crosslink degree and high branch degree in the macromolecules are favorable to improve the solubility of polymers, and ratio of raw materials is one important factor to determine the structure of macromolecules. Infrared spectra of samples 1, 6, and 8 are

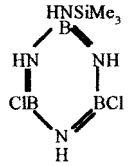
Table II Data Processing of the Poly(borazinylamine) Synthesis Experiment

	Experiment Plan			Experiment Result			
No.	Temperature (°C)	Solvent	Ratio of Raw Material	Mark of Solubility	Mark of Synthesis Yield (%)	Mark of Ceramic Yield (%)	Average Yield (%)
1	1	1	1	0	2.9	9.2	4.0
2	1	2	2	10	3.5	6.9	6.8
3	1	3	3	0	2.4	9.6	4.0
4	2	1	2	10	8.0	8.0	8.7
5	2	2	3	0	5.3	6.5	3.9
6	2	3	1	0	10	10	6.7
7	3	1	3	5	8.7	8.7	7.5
8	3	2	1	0	8.6	3.7	4.1
9	3	3	2	0	7.7	7.8	5.2
Total mark sum for the same level of each factor:				$T = 25$	$T = 57.1$	$T = 70.4$	$T = 50.9$
S_{o1}	10	15	0				
S_{o2}	10	10	20				
S_{o3}	5	0	5				
R_{so}	5	15	20				
S_{y1}	8.8	19.6	21.5				
S_{y2}	23.3	17.4	19.2				
S_{y3}	25	20.1	16.4				
R_{sy}	16.2	2.7	5.2				
C_1	25.7	25.9	22.9				
C_2	24.5	17.1	22.6				
C_3	20.2	27.4	24.8				
R_C	5.5	10.3	2.2				
A_1	14.8	20.2	14.8				
A_2	19.3	14.8	20.5				
A_3	16.7	15.8	15.4				
R_A	4.5	5.3	5.7				

Sample 6, which has the highest synthesis yield and ceramic yield, gets a 10 score. The others get their score by proportion. Solution samples get a 10 score; dissoluble samples get a 0 score. S_0, mark of solubility; S_y, mark of synthesis yield; C, mark of ceramic yield; A, average mark; R, maximum margin. Subscripts 1, 2, and 3 indicate different levels.

almost the same (see Figure 4), suggesting raw materials in the same ratio [TCB : $(Me_3Si)_2NH$ = 1 : 1]. Whereas the raw materials ratio of sample 4 is TCB : $(Me_3Si)_2NH$: BCl_3 = 1 : 6 : 1; hence, the infrared peaks at 1100–1000 cm^{-1} and 820 cm^{-1} are obviously different from the others. Thus, it manifests that the raw materials ratio is the substantial factor that influences the structure and solubility of poly(borazinylamine).

There are three B—Cl bonds in each TCB molecule, which act as functional groups. When TCB and $(Me_3Si)_2NH$ are in the ratio 1 : 1, the obtained polymer is in high B-three-dimensional crosslink degree and with poor solubility. When BCl_3, which is more active than TCB, participates in the aggregation reaction, it will react with $(Me_3Si)_2NH$ producing $(Me_3Si)NHCl$ and $(Me_3SiNH)_2BCl$ first, and then



(I) ring compound. Low crosslink degree poly(borazinylamine), whose solubility was ameliorated remarkably, can be obtained as reactant of (I) and $(Me_3Si)_2NH$.

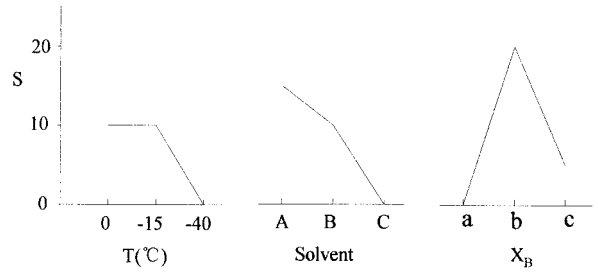


Figure 1 Total mark sum for solubility S versus each level of each factor. A, Cyclohexyl; B, ether; C, chlorobenzene; a, 1 : 1 : 0; b, 1 : 6 : 1; c, 1 : 12 : 3.

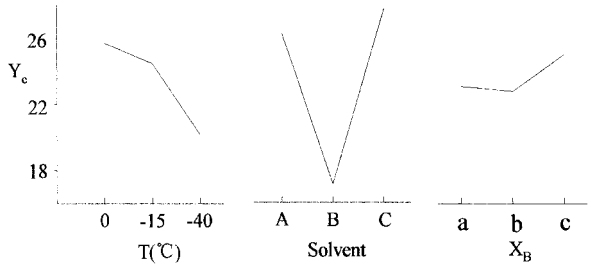


Figure 3 Total mark sum for ceramic yield Y_c versus each level of each factor. A, cyclohexyl; B, ether; C, chlorobenzene; a, 1 : 1 : 0; b, 1 : 6 : 1; c, 1 : 12 : 3.

Effect of Reaction Temperature on the Synthetic Yield of Poly(borazinylamine)

Figure 2 clearly shows that temperature is the most important factor that influences the synthetic yield of poly(borazinylamine). The aggregation process is an exothermic reaction. Low reaction temperature can restrain side reaction and elevate synthetic yield. The extent of yield increase is greater when reaction temperature drops from 0°C to −15°C than from −15°C to −40°C. From the point of operability and energy saving, it is appropriate to react at −15°C.

Effect of Solvent on the Ceramic Yield of Poly(borazinylamine)

As shown in Figure 3, the main factor that influences the ceramic yield of poly(borazinylamine) is solvent. It is not clear how solvent can impact the molecule weight and crosslink degree of the obtained polymer. However, it is apparent that poly (borazinylamine), with the presence of ether, has poor ceramic yield. This is because ether, which is a Lewis base, can change the mechanism of aggregation by forming an additive compound with BCl_3 or TCB via the Lewis acid–base reaction. On the other hand, all poly(borazinylamine)s that got in nonpolar solvent (such as cyclohexane and benzene) or in polar solvent (such as chlorobenzene) had good ceramic yield.

Summarize the aforementioned analysis, the optimal synthetic condition of poly(borazinylamine) is letting TCB, $(Me_3Si)_2NH$, and BCl_3 occur in the ratio of 1 : 6 : 1, using cyclohexane as solvent and keeping the reaction temperature at −15°C.

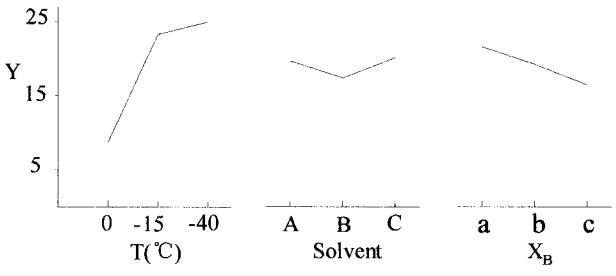


Figure 2 Total mark sum for synthesis yield Y versus each precedent of each factor. A, Cyclohexyl; B, ether; C, chlorobenzene; a, 1 : 1 : 0; b, 1 : 6 : 1; c, 1 : 12 : 3.

Characterization of the Molecular Structure of Poly(borazinylamine)

In Figure 4, the absorption at 3400–3500 cm^{-1} and 1660 cm^{-1} attributes to the bridging N—H bond. The peak at 3100–3200 cm^{-1} (N—H), 1465–1330 cm^{-1} (B—N), and 700 cm^{-1} (characteristic absorption of BN hexagon) are all due to groups of the BN hexagon. At 1040 cm^{-1} is the

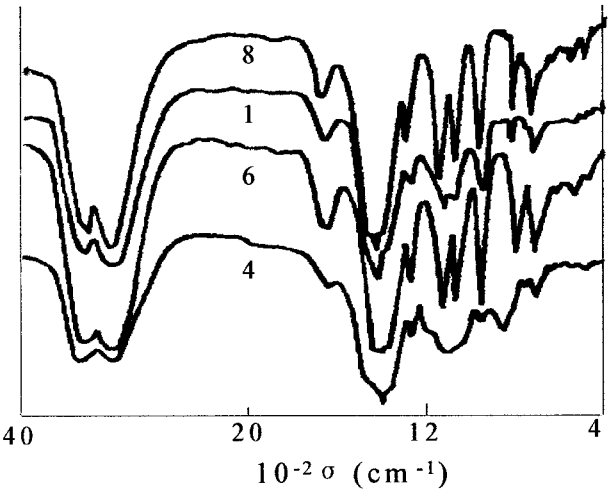


Figure 4 Infrared spectrum of polyborazine samples 1, 4, 6, and 8.

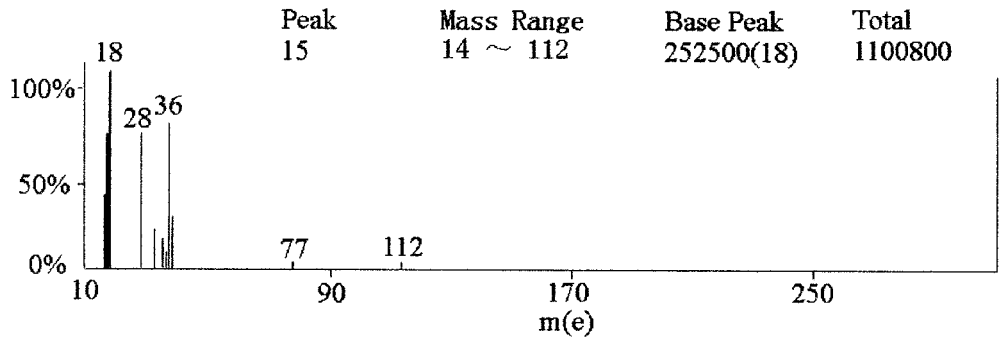
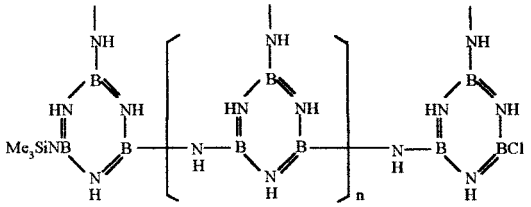


Figure 5 Mass spectroscopy spectrum of poly(borazinylamine) sample 6.

vibrational absorption of B—Cl bonds in terminal groups. The absorption at 940 cm^{-1} and 800 cm^{-1} are caused by the $\overset{\text{H}}{\underset{}{—\text{NSiMe}_3}}$ terminal. The structure formula of poly(borazinylamine) can be surmised as:



Because sample 6 is a three-dimensional or B-crosslinked reticulated polymer, there is no molecular or ionic peak of poly(borazinylamine) in Figure 5. The obtained mass spectrum ascribes to the released small molecules during pyrolysis of poly(borazinylamine).[5]

Summarizing infrared and mass spectroscopic analyses, the molecule structure formula of poly(borazinylamine) can be ascertained as formula (II).

Pyrolysis Property of Poly(borazinylamine)

The pyrolysis property of poly(borazinylamine) was investigated by DTA, TG and infrared analyses. As shown in Figure 6: (1) During heat treatment, no obvious exothermal process was observed. It manifests that volatilization of solvent and molecule fragment disbonded from branch chain occurs during the heat treatment of the aggregation product. Below 200°C, the endothermic peak was assigned to the volatilization of solvent and small molecules. Between 200° and 300°C, disbondment of macromolecule happens and molecule fragments volatilize. (2) Except for sample 2, the higher the crosslinking degree, the higher the ceramic yield and corresponding temperature of endothermic peak that suggests disbondment. The DTA-TG curves of sample 6 (Figure 7) show 18% weight loss and a wide endothermal peak below 180°C, which may ascribe to the volatilization of Me_3SiCl and unevaporated solvent. There are two endothermal peaks and 38% weight loss between 200° and 300°C, suggesting disbondment of bridging group in the polymer and release of small molecules. From 340° to 1000°C, no obvious heat exchange reaction was observed; there is only 6% weight loss because of a small amount of H_2. After sintering at 1000°C, organic groups in the synthetical poly(borazinylamine) almost disappeared; the h-BN hexagon ring was obtained. This can be confirmed by Figure 8. In Figure 8 (no. 2), the strong absorption at 1465–1330 cm^{-1} ascribes to B—N stretching vibration. The absorptions at 1200 cm^{-1} and 940 cm^{-1} were assigned to a small quantity of Si—C

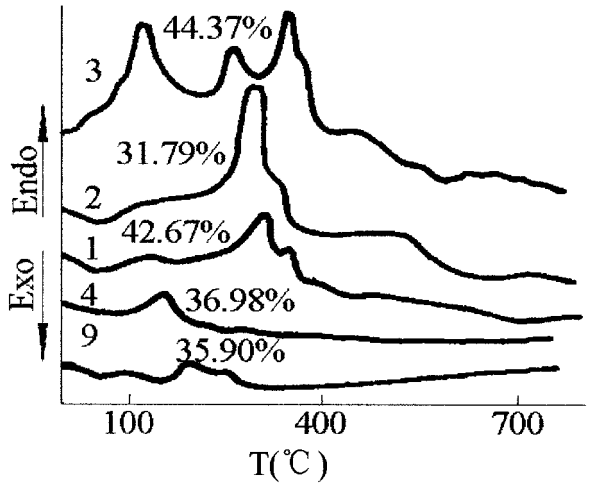
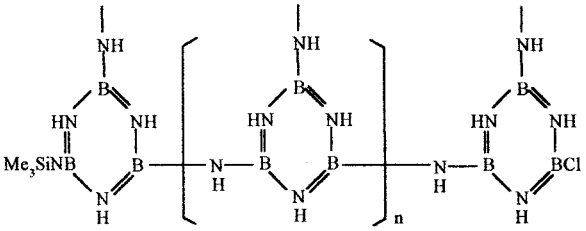


Figure 6 DTA curve of poly(borazinylamine) samples 1, 2, 3, 4, and 9. The % number was ceramic yield of the sample.

and Si—N, respectively. Thus, it can be concluded that pyrolysis of poly(borazinylamine) at 1000°C gives hexagonal h-BN and small amount of SiC and Si_3N_4.

CONCLUSIONS

1. Poly(borazinylamine) was synthesized from an aggregation reaction of TCB, $(Me_3Si)NH$, and BCl_3. By means of infrared and mass spectroscopic analyses, the structure of the polyborazine was identified as follows:



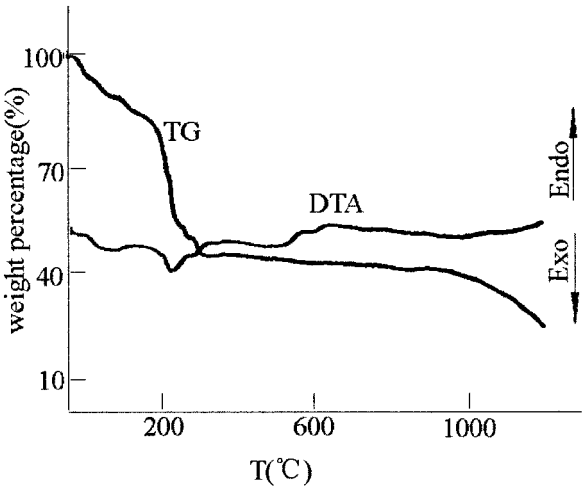


Figure 7 DTA-TG curve of poly(borazinylamine) sample 6.

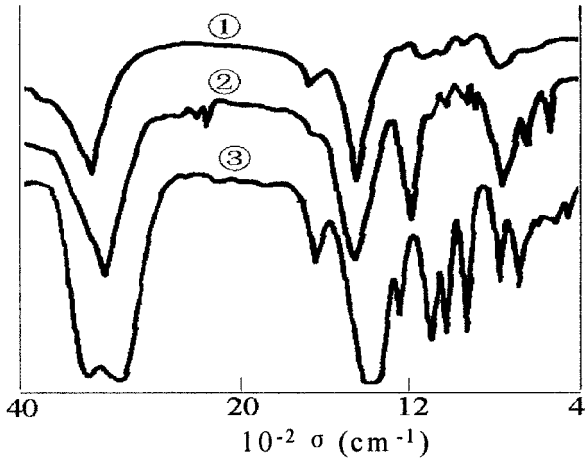


Figure 8 Infrared spectrum of 6 samples preceding and after sintering. ①, Pure BN powder; ②, sample 6 after sintering; ③, sample 6 preceding sintering.

2. The synthetic yield of poly(borazinylamine) can be increased by lowering the reaction temperature. Poly(borazinylamine)'s solubility mainly depends on the raw materials ratio. The solvent has a great effect to the ceramic yield of poly(borazinylamine).
3. Thermal decomposition of poly(borazinylamine) accompanying gas evolution is essentially complete at 350°C. Continued pyrolysis of poly(borazinylamine) produce hexagonal h-BN at 1000°C.

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