

Thermal Stability and Molecular Weight of Two New Boron-Nitrogen Polymers

S. Y. PUSATCIOGLU, H. A. MCGEE, JR., A. L. FRICKE, and J. C. HASSLER, *Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

Synopsis

Molecular weight and thermal stability measurements on the presumed polymers of aminoborane, H_2BNH_2 , and aminodifluoroborane, F_2BNH_2 , were explored using a laser light scattering technique for the molecular weight measurements and both differential thermal analyses and thermogravimetric analyses for the thermal stability studies. Weight-average molecular weight of polymeric aminodifluoroborane in water was determined as 23,000 g/mole, whereas the molecular weight of polymeric aminoborane could not be determined since a suitable solvent was not found. Both DTA and TGA observations showed partial decomposition of polymeric aminoborane between 135° and 200°C, and the vaporization of polymeric aminodifluoroborane between 250° and 360°C.

INTRODUCTION

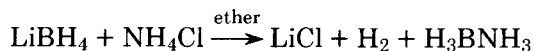
Because the B-N pair is isoelectronic with C_2 , a chemistry paralleling organic chemistry is to be expected, and many analogs have been synthesized and characterized. Certain of these compounds could, in principle, form thermally stable inorganic polymers. Among these, the ethylene-like aminoborane which is the principal compound of the aminoborane family, H_2BNH_2 , and aminodifluoroborane, H_2NBF_2 (analogous to 1,1-difluoroethylene), have been thought to form polymeric materials under proper conditions.

The probable existence of these polymeric materials has been reported by most investigators who have studied elementary compounds of boron and nitrogen. However, few attempts have been made to characterize the polymeric aminodifluoroborane with the exception of a previous study recently reported from this laboratory.¹ On the other hand, previous studies of polymeric aminoborane are inconsistent, and ambiguities of characterization still remain since the compounds might also be merely condensation products of 2 to 5 monomeric units rather than true polymeric products. Hence, it seemed reasonable that polymer characterization techniques might be applied to characterize these very interesting compounds. Therefore, a laser light scattering technique was developed and used to determine the molecular weight of these polymers, and both differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed to study the thermal stability of the materials.

EXPERIMENTAL

Polymerization of $(\text{H}_2\text{BNH}_2)_n$ and $(\text{F}_2\text{BNH}_2)_n$

$(\text{H}_2\text{BNH}_2)_n$. Monomeric aminoborane was produced by the vapor-phase pyrolysis of ammonia borane which was obtained by the reaction



Monomeric aminoborane is stable in the condensed phase only at very low temperatures.² It was converted into the polymeric form in an uncontrolled manner by merely allowing the solid monomer to warm from its temperature of condensation of 77 K.

$(\text{F}_2\text{BNH}_2)_n$. Polymeric aminodifluoroborane was prepared by the low-temperature condensation (77 K) of the monomer that was formed from the pyrolysis of ammonia-trifluoroborane at 185°C. The adduct was produced from trifluoroborane etherate and ammonia in diethyl ether solution.

More details on these preparations are available in recently published papers.^{1,2}

Thermal Analysis

Thermal stability of the materials was studied using a du Pont differential thermal analyzer, Model 900, and a du Pont thermogravimetric analyzer, Model 950. For all DTA studies, a standard DTA cell was used, and both DTA and TGA analyses were performed in a nitrogen atmosphere. In the DTA analyses, the materials were heated from room temperature to 400–500°C at a rate of 20°C/min, and they were cooled by natural heat loss with the heater turned off but with the nitrogen gas cover maintained at the same flow rate of 2 std. cu. ft./hr. In the TGA analyses, the samples were heated at a rate of 15°C/min from room temperature to 500–1000°C.

Molecular Weight Determination

A new laser light-scattering device was designed and constructed for these measurements, and it has been described in detail in a recent paper.³ However, these measurements on BN polymers were made using a 5 mW neon laser light source (6328 Å) rather than the 100 mW He–Cd laser (4420 Å) as described there. The instrument takes advantage of recently developed silicon photodiodes as light detectors to allow a direct readout of the ratio of intensities of the scattered and incident beams for dilute polymer solutions. To determine the molecular weight of these materials, all of the scattering measurements were taken only at an angle of 90° relative to incident beam while varying the concentrations of materials. Experiments revealed that the scattering intensities of the solutions were symmetric about this angle.

A Brice–Phoenix Model BP-2000-V differential refractometer was used to determine the differences in the refractive indices of the polymer solutions and their solvent. The only modification made on this instrument was the use of the neon laser light source rather than the original mercury arc source.

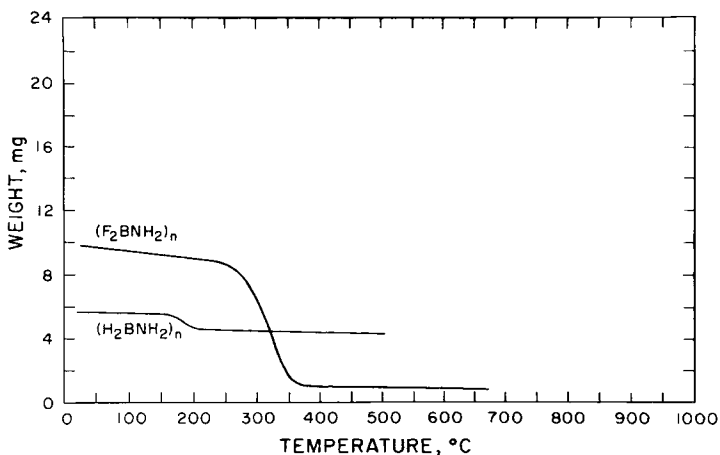


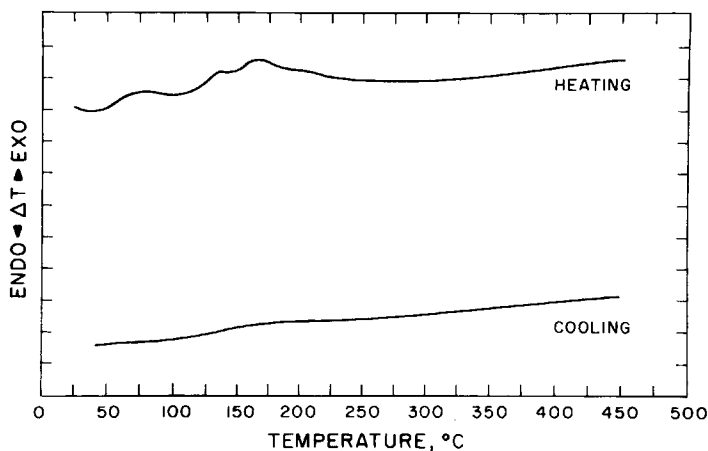
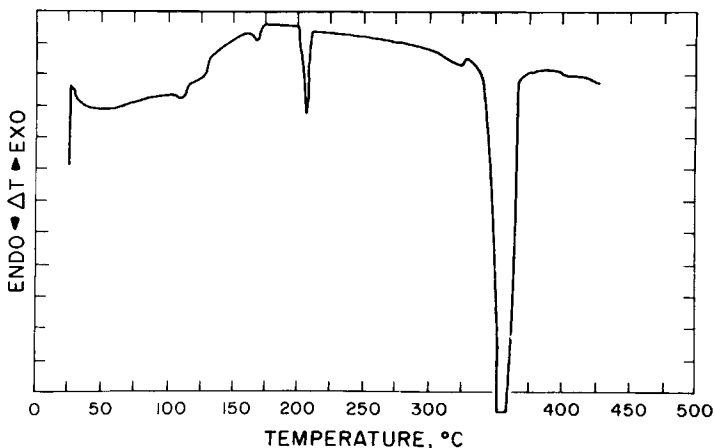
Fig. 1. TGA thermogram of $(H_2BNH_2)_n$ and $(F_2BNH_2)_n$.

Since suitable solvents for either material were unknown, qualitative solubility tests were conducted to select proper solvents. This is a task of major importance that is an essential preliminary to any light scattering analysis. Also, great care was exercised in the clarification of the solutions and solvent; each was centrifuged and filtered through a 2.5- μ m filter, the filtrate receiver was covered with a septum, and the sample was subsequently withdrawn for transfer to the scattering cell using a needle and syringe.

RESULTS AND DISCUSSION

Thermal Analysis

Volatilization and decomposition occurred on heating both materials, for the TGA showed a loss of mass for both polymers with increasing temperature in regions where the DTA results showed exothermic and endothermic process for $(H_2BNH_2)_n$ and $(H_2NBF_2)_n$, respectively. The polyaminoborane, $(H_2BNH_2)_n$, partially decomposed at a rate more or less linear with temperature between about 170° and 200°C while about 77% of the material remained as a white solid product resembling boron nitride (Fig. 1). No further change was observed in the thermolysis of the material upon continued heating from 200° to 1000°C. Mass-spectral analysis of the vapor that was evolved suggested the evolution of H_2 and borazine. The observed loss of mass is in agreement with the assumption that all of the hydrogens in $(H_2BNH_2)_n$ were volatilized upon heating the material to 200°C to leave behind only solid boron nitride, $(BN)_n$. Recent protolysis studies⁴ suggested the existence of two types of hydrogen in polymeric aminoborane if it is assumed to be chain-like, hydridic hydrogens on quaternary boron — BH_2 — within the chain which were rapidly attacked, and hydridic hydrogens on a terminal — BH_2 which were attacked much more slowly. This is also suggested by the DTA analyses performed in this work where we have observed two separate exothermic transitions occurring at about 137° and 170°C (Fig. 2). The exothermic transition observed between 50° and 90°C by DTA was likely due to the evolution of residual borazine vapor. Borazine⁵ is a clear colorless liquid,

Fig. 2. DTA thermogram of $(\text{H}_2\text{BNH}_2)_n$.Fig. 3. DTA thermogram of $(\text{F}_2\text{BNH}_2)_n$.

mp -58°C , bp 55°C , and it could have been present in a small amount in the original polymeric material. Although the change in slope was small, a second-order transition was observed at 175°C upon cooling the material from 450°C . This could be interpreted as a solid-phase transition of boron nitride at this temperature, perhaps the hexagonal-to-cubic transformation that is already well known for this material.

The aminodifluoroborane product, $(\text{F}_2\text{BNH}_2)_n$, almost totally vaporized at a linear rate with temperature between about 250° and 360°C , and only about 8% of the material remained as a blackish powder (Fig. 1). The material undergoes a continuous exothermic reaction during heating from room temperature to 175°C , as shown by DTA analysis (Fig. 3). TGA analysis showed continuous weight loss for the material over this range, and mass-spectral analysis revealed trifluoroborazine and aminodifluoroborane as volatile products. Discounting the possibility of an exact coincidence of transition temperatures,

the formation of NH_4BF_4 in the thermolysis of the polymer is shown by the characteristic sharp transition which appeared at 206°C .

Light Scattering Analysis

It was difficult to produce solutions of $(\text{H}_2\text{BNH}_2)_n$ since the substance was essentially insoluble in all solvents. Each of these solutions in the solubility tests was heated no higher than 75°C since the TGA analyses revealed that the material starts to decompose near 100°C . Aniline, DMF, DMSO, and liquid ammonia were the only solvents that seemed to dissolve at least a portion of the polymer among more than 40 candidate solvents that were tested. However, infrared spectra of these solutions in DMF, aniline, and DMSO failed to reveal any of the known bands of the solute² due to its very low concentration in the solutions because of its very low solubility. On the other hand, the solubility of the material in liquid ammonia was not clearly established. DMSO was chosen as the best solvent for use in the light scattering analysis because (1) somewhat more of the solid actually dissolved in DMSO than in other solvents, and (2) DMSO is known to dissolve most of the cycloborazenes. However, the solubility of $(\text{H}_2\text{BNH}_2)_n$ in DMSO (~ 0.08 g/100 ml solution) was too low to produce an efficient scattering intensity from the solution, and the light scattering measurements on this polymer were abandoned.

The polymeric aminodifluoroborane, $(\text{F}_2\text{BNH}_2)_n$, dissolved very rapidly in cold water, and solubility without reaction was confirmed when the same DTA spectrum was observed from the material recrystallized from water as for the original polymer itself.

The scattering ratios measured for $(\text{F}_2\text{BNH}_2)_n$ were summarized in Table I with the other light scattering results, and the determination of the molecular weight appears in Figure 4. The measured values of the ratio of the output voltages, E_2/E_1 , from the photodiodes receiving the scattered and incident beams were converted to values of the ratio of the intensities of the scattered and incident beams, I_{90°/I_0 , by the relation

$$\frac{I_{90^\circ}}{I_0} = k \frac{E_2}{E_1}$$

TABLE I
Light Scattering Results for $(\text{F}_2\text{BNH}_2)_n^a$

Concentration, g/ml	$(E_2/E_1) \times 10^{10}$	$(Kc/R_{90^\circ}) \times 10^5$
0.004889	7.95	1.1180
0.004191	4.78	1.5939
0.003668	4.15	1.6102
0.002934	3.45	2.3070

^a Weight-average molecular weight, 22,831 g/mole (rounded to 23,000 in text); second virial coefficient, -0.345×10^{-2} ml-mole/g²; Rayleigh ratio at 90° , $R_{90^\circ} = \frac{I_{90^\circ}}{I_0} \frac{r^2}{V} = \frac{E_2}{E_1} k \frac{r^2}{V}$, cm⁻¹; refractive index concentration gradient, $dn/dc = 0.0325$, ml/g; optical constant, $K = 3.799 \times 10^{-9}$, cm² mole/g².

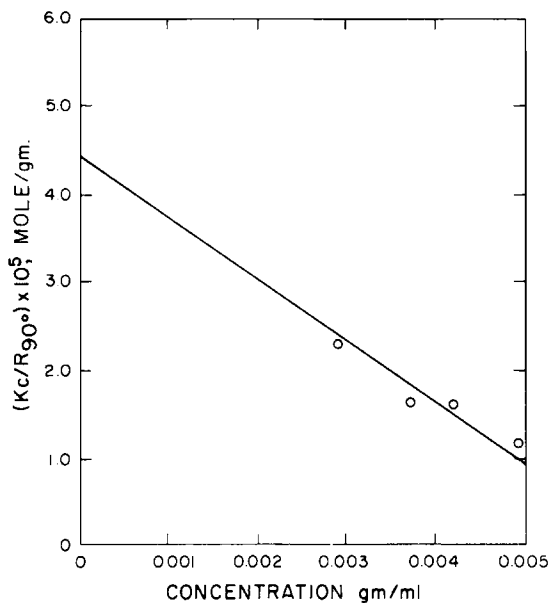


Fig. 4. Determination of molecular weight of $(F_2BNH_2)_n$.

where k is a proportionality constant which was determined using a solution of 12-tungstosilicic acid (MW 2879) as a standard. This compound was chosen because its light scattering properties were well known; it has a high molecular weight, and it is highly soluble.⁶ The molecular weight of the $(H_2NBF_2)_n$ was determined as 23,000 g/mole with a total maximum experimental and instrumental error of 19%. Further developments on the new light scattering device in this laboratory will allow a decrease in this instrumental error.

Because the polymer molecules are small and presumably optically isotropic, the depolarization will likely be small. Even if 1% depolarization occurs, the Cabannes factor $(6 - 7\rho)/(6 + 3\rho)$, where ρ is the fraction depolarized, would suggest a molecular weight less than 2% smaller than that calculated in Table I.

CONCLUSIONS

Both DTA and TGA studies of $(H_2BNH_2)_n$ and $(F_2BNH_2)_n$ showed that both materials start to vaporize and decompose upon heating near 100°C. Polymeric aminoborane partially decomposed between 135° and 200°C, most likely with the evolution of hydrogen, and 77% of the material remained as a white solid product that was presumedly boron nitride. On the other hand, polymeric aminodifluoroborane vaporized between about 250° and 360°C with only 8% of the material remaining as a blackish powder. The formation of NH_4BF_4 in the thermolysis was indicated by the characteristic peak in the DTA curve at 206°C.

The relatively high molecular weight measured for $(F_2BNH_2)_n$ confirmed the polymeric character of the material that may be formed in an uncontrolled

manner by condensing the monomer. The existence of polymeric aminoborane remains to be established since its molecular weight could not be determined because of the insolubility of that material.

The authors would like to thank the National Science Foundation for their support of this work through Grant GK-34541. This discussion was abstracted from a thesis by S. Y. Pusatcioglu submitted in partial fulfillment of the requirements for the M.S. Degree in Chemical Engineering (February 1975).

References

1. E. F. Rothgery, H. A. McGee, Jr., and S. Pusatcioglu, *Inorg. Chem.*, **14**, 2236 (1975).
2. C. T. Kwon and H. A. McGee, Jr., *Inorg. Chem.*, **9**, 2458 (1970).
3. S. Pusatcioglu, A. L. Fricke, H. A. McGee, Jr., and J. C. Hassler, to be submitted to *Rev. Sci. Inst.*
4. D. L. Denton, H. D. Johnson, II, C. W. Hickam, Jr., R. K. Bunting, and S. G. Shore, *J. Inorg. Nucl. Chem.*, **37**, 1037 (1975).
5. Kurt Niedenzu and John W. Dawson, *Boron-Nitrogen Compounds*, Springer-Verlag, New York, 1965.
6. M. Kerker, *The Scattering of Light and Other Electromagnetic Radiation*, Academic Press, New York, 1969.

Received April 5, 1976

Revised April 27, 1976