

Thermal decomposition of polymeric aminoborane (H₂BNH₂)_x under hydrogen release

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Abstract

Polymeric aminoborane (H₂BNH₂)_x has been isolated during the thermal decomposition of solid borazane H₃BNH₃ at temperatures below 370 K. Polymeric aminoborane is a white noncrystalline solid, stable at room temperature and up to 380 K. In the temperature range of 380–500 K polymeric aminoborane undergoes a thermal decomposition, which was studied by differential scanning calorimetry (DSC), by thermogravimetry (TG) and by volumetric measurements. The solid residue was characterized by IR spectroscopy, by powder X-ray diffraction (XRD) analysis and by solid state ¹¹B NMR spectroscopy.

The thermal decomposition of polymeric aminoborane (H₂BNH₂)_x is an exothermic process accompanied by evolution of nearly 1 mol hydrogen per mole H₂BNH₂ unit corresponding to the volumetric measurements. The detected mass loss of the solid phase indicates the formation of further gaseous products beside hydrogen. The final mass loss increases with rising heating rate, in contrast to the final amount of evolved hydrogen, which still remains constant.

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1. Introduction

BNH-compounds are of great interest as materials for the use as hydrogen storage systems. A suitable hydrogen source could be borazane H₃BNH₃, which is a white crystalline solid with a hydrogen content of 19.5 wt.% [1,2]. In order to realize the formation and decomposition reactions in the BNH-system with the exchange of hydrogen, it seems at first necessary to have reliable information about the thermo chemical properties and the mechanism of the decomposition process.

Borazane releases hydrogen during a thermal decomposition at temperatures below 500 K [3]. There are two partially overlapping exothermic effects [3], associated with the evolution of hydrogen. In our previous investigation [4] we showed that both steps of borazane decomposition could be separated, if adequate experimental conditions are cho-

sen. The thermal decomposition under isothermal conditions at temperatures between 343 and 363 K as well as under non-isothermal conditions at heating rates far below 0.5 K min⁻¹ leads to the complete termination of the first decomposition step before the start of the second decomposition step. This first decomposition step was characterized by scanning calorimeters (DSC), with thermogravimetric (TG) and volumetric measurements. Elemental analysis, XRD and FTIR spectroscopy show that the white solid residue after the first decomposition step is polymeric aminoborane (H₂BNH₂)_x.

In the present work results for the thermal decomposition of polymeric aminoborane (H₂BNH₂)_x are given.

Earlier the thermal decomposition of polymeric aminoborane was investigated by Geanangel et al. [5] by means of TG and DSC. But aminoborane sample used by Geanangel et al. [5] obviously had a non uniform composition, which lead to a strong influence of the sample history on the obtained TG data.

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We have prepared well defined samples of polymeric aminoborane by controlled thermal decomposition of solid borazane H_3BNH_3 .

The decomposition was carried out and investigated in temperature range between 300 and 500 K by the use of differential DSC, TG and volumetric measurements. The influence of the heating rate on the thermal decomposition was considered. The solid decomposition product was characterized by investigations with different standard methods.

2. Experimental

The polymeric aminoborane was prepared by the thermal decomposition of borazane at $T = 363$ K. Borazane was synthesized by reaction of ammonium carbonate and sodium borohydride in a solution of tetrahydrofuran according to a method described by Hu et al. [6].

Calorimetric measurements were performed in a DSC C80-device and a DSC 141 both from Setaram. Measurements in the DSC 141 were carried out under nitrogen atmosphere at heating rates between 0.5 and 10 K min^{-1} .

In DSC C80 the aminoborane was decomposed under nitrogen atmosphere at a heating rate of 0.1 K min^{-1} . These investigations at a gas flow (10 ml min^{-1}) were performed using the calorimetric vessel for gas circulation. For measurements at different gas pressures (1–80 bar) a high pressure vessel was used. The typical sample mass at the experiments was $m = 20$ mg.

Volumetric measurements were carried out by coupling a DSC 111 from Setaram with an equipment for gas-volumetric measurements. The heat flow and the volume of the released hydrogen were recorded simultaneously. With the volumetric equipment only such gases are detected, which do not condense at room temperature and which are not soluble in water.

The TG measurements were performed in the TG/DSC 111 from Setaram under argon atmosphere at different heating rates. The sample mass was about 6 mg.

The elemental analysis of the solids was carried out with the Herraues Analyser CHN-O-Rapid. IR spectroscopy data were obtained with a Fourier Transformed IR Spectrometer 510 (Nicolet) using KBr-pellets. For X-ray powder diffraction analysis a diffractometer D 5000 (Siemens) was used. Solid ^{11}B NMR investigations were performed by means of a MSL 300 MHz spectrometer (Bruker).

3. Results and discussion

3.1. Calorimetric, thermogravimetric and volumetric investigations with varying heating rate

Typical results of the calorimetric investigations of the aminoborane decomposition in the temperature range from 370 to 510 K are shown in Fig. 1. The temperature depen-

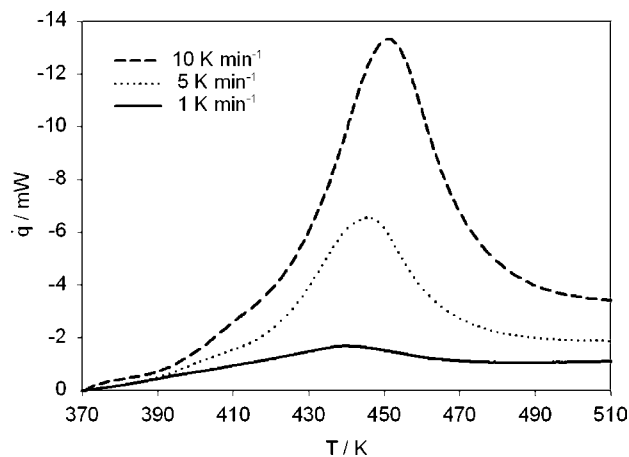


Fig. 1. Heat flow for the thermal decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ in dependence on the temperature (Setaram DSC 141, nitrogen flow, heating rates 1, 5 and 10 K min^{-1}).

dences of the heat flow at the heating rates of 1, 5 and 10 K min^{-1} are represented. DSC measurements do not show any heat evolution below 380 K. This fact indicates that the first step of the borazane decomposition is finished completely and that the polymeric aminoborane is stable up to this temperature.

With increasing temperature an exothermic process attributed to the thermal decomposition of polymeric aminoborane starts near $T = 388$ K. The comparison of the recorded heat flow with the constructed base line leads to the conclusion that with rising heating rate an increase of the final temperature for the decomposition or a characteristic decomposition time are observable.

Geanangel et al. [5] and Kim et al. [7] have studied the thermal decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ by means of DSC measurements also. In the temperature range from 330 to 500 K several exothermic peaks were observed. A significant difference to our results consists in the occurrence of exothermic events at temperatures below 370 K in DSC curves measured by Kim et al. [7] and in the two exothermic steps in the temperature range between 370 and 470 K measured by Geanangel et al. [5]. This is probably due to differences in the composition between the samples investigated by [5,7] and in our work. The polymeric aminoborane investigated by Kim et al. was a co-product of the synthesis of borazine from NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$ in tetraglyme solution near 400 K. Volatile products were pumped into a trap filled with liquid nitrogen. Borazine has been evaporated from the mixture in the trap and the remaining white powder was the investigated sample of polymeric aminoborane. Geanangel et al. [5] applied a white coating of the liquid nitrogen filled cold finger, formed during the thermal decomposition of borazane at 400 K. It could be expected, that the samples used by Geanangel et al. contains sublimated borazane. For our investigations we used samples of polymeric aminoborane which were prepared by the thermal decomposition of borazane at 363 K. These samples of polymeric aminoborane had a well

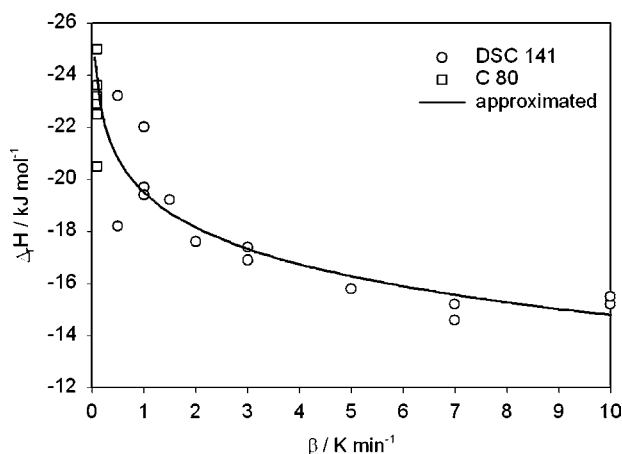


Fig. 2. Values of the decomposition enthalpy for polymeric aminoborane in dependence on the heating rate.

defined composition, which was proved by analytical methods. Calorimetric, gravimetric and volumetric experiments, which were performed with different samples of polymeric aminoborane, do not show any significant influence of sample preparation.

The molar decomposition enthalpy values $\Delta_r H$ determined for polymeric aminoborane from the DSC curves are given in Fig. 2 in dependence on the heating rate β . Especially at heating rates lower than 3 K min^{-1} a rise of the $\Delta_r H$ values with decreasing heating rate is observable.

When decomposition of aminoborane was performed at $\beta = 10 \text{ K min}^{-1}$ an enthalpy value of $\Delta_r H = -(15.4 \pm 1.2) \text{ kJ mol}^{-1}$ was determined. The value for the same quantity was at $\beta = 0.1 \text{ K min}^{-1}$ equal to $\Delta_r H = -(23.9 \pm 2.4) \text{ kJ mol}^{-1}$.

The observed dependence of the decomposition enthalpy is probably a consequence of several contributions from different reaction paths to the total process. Different decomposition products are probable in dependence on the heating rate. From the results of TG/FTIR and TG/MS investigations [8] followed, that the gas phase at the thermal decomposition of borazane contains monomeric aminoborane H_2BNH_2 , borazine $\text{B}_3\text{N}_3\text{H}_6$ and small amounts of diborane B_2H_6 in addition to hydrogen. The evolved amount of monomeric aminoborane and borazine increases with rising heating rate especially during the second decomposition step [8].

The amount of released hydrogen during the thermal decomposition of polymeric aminoborane was recorded by means of volumetric measurements. Further volatile decomposition products, such as monomeric aminoborane H_2BNH_2 , borazine $\text{B}_3\text{N}_3\text{H}_6$ and diborane B_2H_6 , were not detected by the used volumetric equipment. These products are condensed or dissolved at room temperature in a trap. Fig. 3 shows the released amount of hydrogen per mol H_2BNH_2 in dependence on the temperature. There are typical curves obtained at different heating rates ($1, 5$ and 10 K min^{-1}).

The evolution of hydrogen starts at approximately $T = 395 \text{ K}$. The released volume of hydrogen is correlated

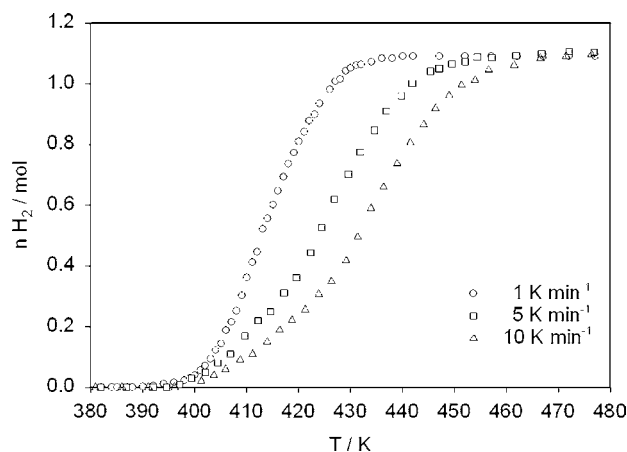


Fig. 3. Amounts of hydrogen released at the decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ in dependence on the temperature (volumetric equipment, nitrogen atmosphere, heating rates $1, 5$ and 10 K min^{-1}).

clearly to the heat power measured with the DSC arrangement. The final amount of released hydrogen is $1.1 \pm 0.1 \text{ mol H}_2$ per mole H_2BNH_2 unit. This result is independent of the heating rate.

Thermogravimetric investigations (TG) deliver the mass loss of the solid sample. In contrast to volumetric measurements this mass loss data are sensitive to the evolution of all gaseous decomposition products.

Typical TG-curves for the decomposition of polymeric aminoborane at different heating rates ($1, 5$ and 10 K min^{-1}) are shown in Fig. 4. A single mass loss step was observed at all used heating rates. It is clearly evident that a mass loss is detectable in the same temperature range, in which hydrogen release and heat evolution were determined.

The final value of the mass loss depends on the used heating rate significantly. With rising heating rate the final mass loss increases from $7.1 \text{ wt.}\%$ at $\beta = 0.1$ to $20.3 \text{ wt.}\%$ at $\beta = 10 \text{ K min}^{-1}$. At a heating rate of 10 K min^{-1} a compar-

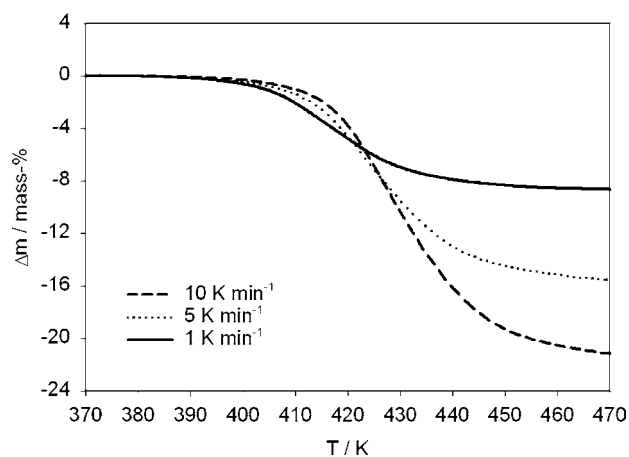


Fig. 4. Mass loss at the thermal decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ in dependence on the temperature (Setaram TG/DSC 111, argon flow, heating rates $1, 5$ and 10 K min^{-1}).

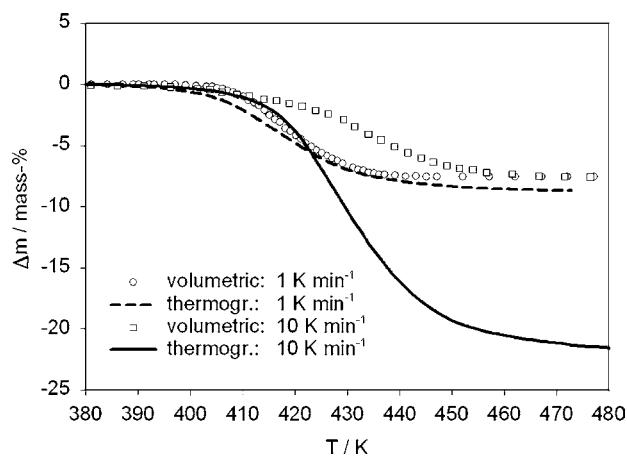


Fig. 5. Experimental data for the mass loss (TG, line) in comparison with the mass loss data calculated from the released amount of hydrogen (volumetric measurements, points), (heating rates 1 and 10 K min⁻¹).

ble final mass loss value of 25 wt.% was observed by Kim et al. [7].

At the same heating rate mass loss values between 13.5 and 32 wt.% are observed by Geanangel et al. [5] in dependence of the sample history. The authors assumed that polymeric aminoborane decomposed to hydrogen and boron nitride in three steps.

A described formation of boron nitride at a temperature of 500 K [5] is not probable, as follows from the volumetrically detected release of only 1.1 mol hydrogen per mol H₂BNH₂.

In Fig. 5, results of thermogravimetric and volumetric investigations are compared. Volumetric results were converted into mass loss data. The release of 1.1 mol H₂, which was detected by volumetric investigations, corresponds to a mass loss of 7.6 wt.% only. The results for the mass loss from thermogravimetric and volumetric investigations are nearly in agreement at a heating rate of 1 K min⁻¹. The amount of

gaseous products evolved in addition to hydrogen should be very small at 1 K min⁻¹.

At a heating rate of 10 K min⁻¹ the final mass loss value from the TG-curve differs considerable from the final mass loss value of the volumetric curve. The difference indicates that a significant amount of gaseous products is evolved in addition to hydrogen at higher heating rates. This is also a confirmation of the assumption explaining the heating rate dependence of the decomposition enthalpy.

3.2. Characterization of solid compounds

Polymeric aminoborane (H₂BNH₂)_x is a white solid, stable at room temperature. This compound cannot be characterized by a melting point, since polymeric aminoborane decomposes with rising temperature by the release of hydrogen. From elemental analysis followed a formula of B_{1.0}N_{0.9}H_{3.9}, comparable to the formula of B_{1.0}N_{1.0}H_{4.3} given by Bøddeker et al. [9] and of B_{1.0}N_{1.0}H_{3.9} given by Komm et al. [10] respectively.

The powder X-ray diffraction analysis of polymeric aminoborane (H₂BNH₂)_x does not show any peaks. Thus, XRD data indicates the noncrystalline nature of the solid.

The solid state ¹¹B NMR spectroscopy provides the first information to the structure of (H₂BNH₂)_x. The spectrum (Fig. 6) shows the fast falling off satellites of the four-fold coordinated boron atoms and a pattern of three-fold coordinated boron atoms in the solid sample. Thus, the (H₂BNH₂)_x does not have a unitary structure, like for example a linear polymer.

The obtained solid state FTIR spectrum of polymeric aminoborane is shown in Fig. 7a and the corresponding FTIR data are represented in Table 1 together with published data for cyclic pentameric aminoborane [9] and polymeric aminoborane [7,10].

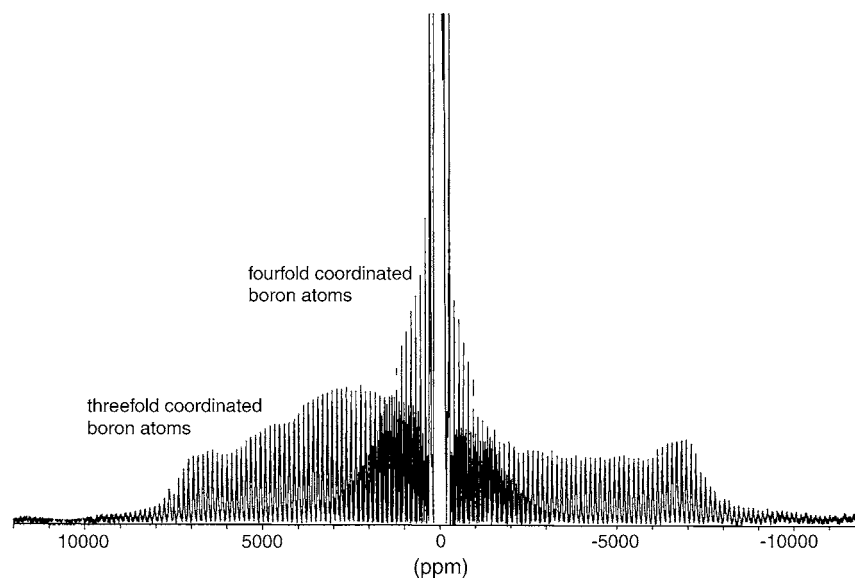


Fig. 6. Solid state ¹¹B NMR spectrum of polymeric aminoborane (H₂BNH₂)_x.

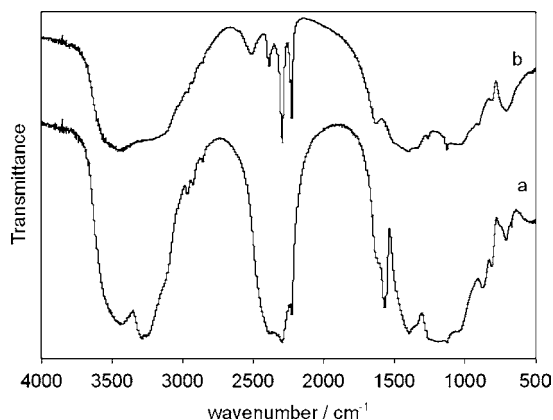


Fig. 7. IR spectra of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ (a) and the $(\text{BNH}_x)_z$ -polymer (b).

The solid residue after the thermal decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ is a white powder. Similar to polymeric aminoborane, the decomposition residue cannot be characterized by a melting point.

Elemental analysis of the decomposition residue leads to a formula of BNH_y with a value of y , which varies from 1.2 to 2.4 in dependence on the decomposition conditions. The higher y -values were observed after the decomposition of aminoborane during 18 h at 473 K and the lower values after a decomposition time of 70 h at the same temperature. Thus, hydrogen contents lower than $y=2$ are given at longer decomposition time. The formation of additional B-N-linkages could cause a higher-condensed net-shaped structure of the solid. In order to indicate the varying structure of the solid decomposition product, it is called as $(\text{BNH}_y)_x$.

From powder X-ray diffraction analysis followed that the $(\text{BNH}_y)_x$ is a noncrystalline solid like polymeric aminoborane.

Table 1
Infrared spectra of aminoboranes

Assignment	$(\text{H}_2\text{BNH}_2)_x^a$ $\bar{\nu}$ (cm^{-1})		$(\text{H}_2\text{BNH}_2)_x^b$ $\bar{\nu}$ (cm^{-1})		$(\text{H}_2\text{BNH}_2)_5^c$ $\bar{\nu}$ (cm^{-1})		$(\text{H}_2\text{BNH}_2)_x^d$ $\bar{\nu}$ (cm^{-1})	
νNH , νNH_2	3300	s	3300	m, s	3301–3250	s	3425–3197	s, sh
νBH , νBH_2	2350	s	2340–2230	m, sh	2420–2300	s	2348	vs
δNH_2	1650, 1500	m	1600	w, br	1572	m	1622	m
νBN			1380	m, s	1412	m	1400	vs
	1260	s	1160	w, br	1205	s	1182	s
					1087	m		
			1040	m, br	1062	m	1068	s
	932	w			973	w		
νBN			850	vw, br	845	w	866	w
νBN	780	w	780, 725	vw			809, 706	w
					650	w		
							576	vw

ν = Stretching, δ = bending.

^a From ref. [7], s: strong, m: medium, w: weak, v: very, sh: shoulder.

^b From ref. [10].

^c From ref. [9].

^d This work.

Table 2
Infrared spectra of borane, polymeric aminoborane, boron nitride and the $(\text{BNH}_x)_z$ -polymer

Assignment	H_3BNH_3^a $\bar{\nu}$ (cm^{-1})	$(\text{H}_2\text{BNH}_2)_x^b$ $\bar{\nu}$ (cm^{-1})	BN^c $\bar{\nu}$ (cm^{-1})	$(\text{BNH}_x)_z$ -polymer ^d $\bar{\nu}$ (cm^{-1})	$(\text{BNH}_x)_z$ -polymer ^e $\bar{\nu}$ (cm^{-1})
νNH_2 , νNH_3	3320–3200	3300		3350	3430 vs
νNH_2					3264 vs
νBH				2500	
νBH_2	2330, 2230, 2130	2330–2230			2389, 2291 vs
δNH_2					1628 sh
δNH_2	1605	1600		1600	1571 s
νBN , γNH_2	1380	1380	1370		1405 m
			1340		
τBH_2	1165	1160		1100–1150	1203 vs
	1065	1040			1058 sh
νBN	790, 735	850, 780, 725	820		871, 820 m

s: Strong, m: medium, w: weak, v: very, sh: shoulder ν = stretching, δ = bending, γ = out of plane, τ = torsion.

^a From ref. [6].

^b From ref. [10].

^c From ref. [11].

^d From ref. [12].

^e This work.

A typical solid state FTIR spectrum of the $(\text{BNH}_y)_x$ is shown in Fig. 7b. The results are nearly identical for samples of different decomposition time.

Characteristic FTIR data for the $(\text{BNH}_y)_x$ are given in Table 2 together with published data for borazane [6], polymeric aminoborane [10], and boron nitride [11]. It seems remarkable that the FTIR spectrum of the $(\text{BNH}_y)_x$ contains peaks, which cannot be attributed only to BH-, NH- and BN-bond. This observation supports the assumption about a net-shaped structure of the compound. Definite statements to the structure of the $(\text{BNH}_y)_x$ was not obtained with these measurements.

4. Conclusion

Calorimetric investigations of polymeric aminoborane, which was prepared by thermal decomposition of borazane at 363 K, pointed out a further thermal decomposition in the temperature range from 380 to 500 K with a formation of a solid residue. The composition of the solid product strongly varies in dependence of the decomposition conditions. The exothermic decomposition enthalpy varies from $\Delta_r H = -(23.9 \pm 2.4) \text{ kJ mol}^{-1}$ for measurements at a heating rate of $\beta = 0.1 \text{ K min}^{-1}$ to $\Delta_r H = -(15.4 \pm 1.2) \text{ kJ mol}^{-1}$ for measurements at $\beta = 10 \text{ K min}^{-1}$.

The thermal decomposition of polymeric aminoborane $(\text{H}_2\text{BNH}_2)_x$ is accompanied by the evolution of different gaseous products as follows by volumetric and thermogravimetric investigations. Hydrogen, monomeric aminoborane, diborane and borazine were observed in the gas phase during the decomposition of the BNH-compounds by means of mass spectroscopy [8]. The final amount of evolved hydrogen ($1.1 \pm 0.1 \text{ mol H}_2$ per H_2BNH_2 unit) is independent of

the used heating rate, the amount of the further volatile decomposition products strongly increase with rising heating rate.

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