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Thermal Decomposition Mechanisms in Poly-Glycidyl Nitrate (PGN) Prepolymer[†]

Sean Maharrey, Aaron Highley, Denielle Weise-Smith, and Richard Behrens
Sandia National Laboratories[‡]
Combustion Research Facility
P.O. Box 969, MS 9052
Livermore, CA. 94551-0969

ABSTRACT

The thermal decomposition of poly glycidyl nitrate (PGN) has been investigated using simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS) and Fourier-Transform ion-cyclotron-resonance (FTICR) mass spectrometry. For this study, unmodified and OH end-modified PGN prepolymer (MW ~4000 Da) were used to investigate the effect of hydroxyl end-modification on the thermal decomposition process. The STMBMS results show that the unmodified PGN prepolymer decomposes over a temperature range of ~100-300°C, with 80% of the sample mass evolving from a rapid decomposition occurring between 195-215°C. The thermal decomposition of PGN is controlled by a reaction process consisting of four pathways: (1) a slow cleavage/decomposition reaction of the CH_2-O-NO_2 functional moiety to form principally CH_2O, NO_2, and NO, a set of two fast reactions of NO with the PGN backbone to form principally (2) HCN, and water, and (3) CO and CO_2/N_2O, and (4) a scissioning/polymerization reaction of the remaining reactive polymer backbone to form the remaining carbonyl functionalized non-volatile residue. The OH end-modified prepolymer thermal decomposition process follows the same four reaction pathways as observed with the unmodified prepolymer.

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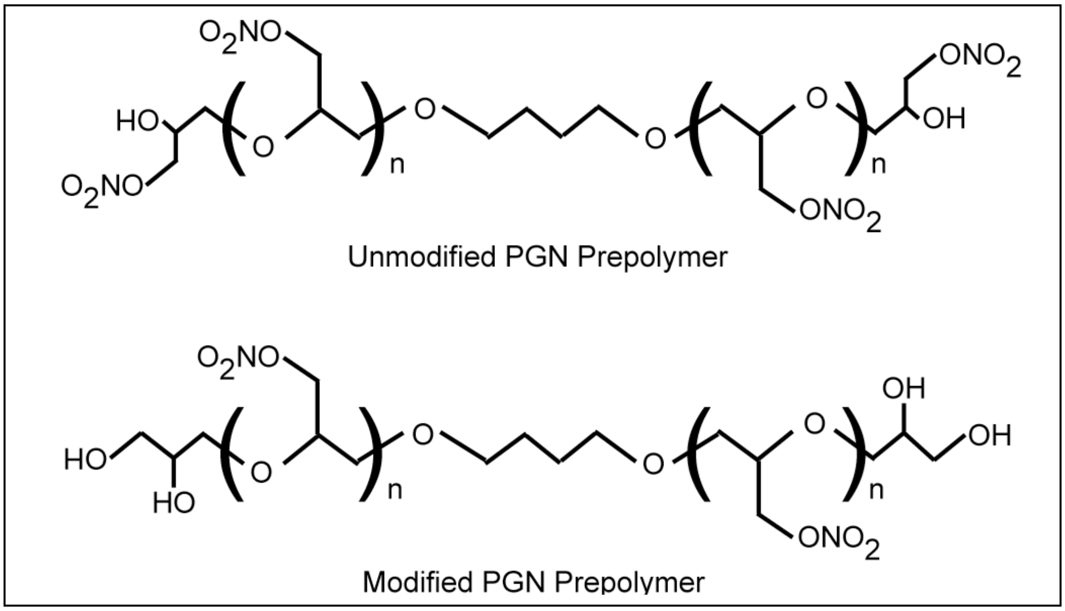
INTRODUCTION

Many current energetic formulations use inert binders. Various energetic binder materials are being investigated in an attempt to increase the energy of explosive and propellant formulations. The nitrate-ester prepolymer PGN (poly-glycidyl nitrate) has high oxygen balance and density, making it the most energetic nitrate ester binder/plasticizer for potential use. However, when PGN is cured using aliphatic isocyanate-derivative curing agents, it exhibits poor aging characteristics. PGN may be a suitable candidate if its properties remain stable after the pre-polymer is cured. To improve long-term stability, both the Defence Evaluation and Research Agency (DERA) and Imperial Chemical Industries (ICI) have used ethylene oxide to end cap the PGN prepolymer with a polyol. Alternatively, researchers at ATK-Thiokol used various aromatic diisocyanates to counter this instability. It is useful to understand if and how this OH end modification process affects stability and the decomposition/combustion kinetics of this energetic binder.



The STMBMS measurements provide time-resolved information on product identities and their rates of formation during the course of thermal decomposition at slower heating rates. This data provides insight into the sequence and rates of bond-breaking events that control the decomposition of PGN. Knowledge gained in understanding the effect that the OH end-modification has on the thermal stability and decomposition mechanism for the PGN prepolymer plays a vital role in determining the long-term stability of isocyanate cured PGN polymer (rubber). Additionally, information gained through this work will also provide insight into how the combustion mechanism/kinetics for a cured PGN formulation can be tailored to meet specific combustion requirements by judicious choice of chemical modification.

Reviews of the literature indicate that previous studies of the decomposition of PGN[1-4] prepolymer have focused on the unmodified prepolymer. Currently, no information is available on the decomposition of an end-modified PGN prepolymer. In this paper, we present a general four-step reaction mechanism for the thermal decomposition of the unmodified PGN prepolymer and a discussion of the effects the OH end-modification has on this reaction mechanism.

EXPERIMENTAL

The STMBMS Instrument

An overview[5] describes the experimental methods and numerical algorithms used to examine and characterize the reactions of energetic materials in the condensed phase at low and moderate temperatures. The details of the simultaneous thermogravimetric modulated beam mass spectrometer (STMBMS) instrument and analysis methods have been described previously.[6-8] The experimental methods utilize: (1) the STMBMS instrument to conduct thermal decomposition experiments and an associated set of numerical algorithms to transform the raw data to rates of formation of the decomposition products, and (2) a Fourier Transform ion cyclotron resonance (FTICR) mass spectrometer to aid in identifying the products.

The basic features of a thermal decomposition experiment using the STMBMS instrument are illustrated in Figure 1. A small sample of PGN prepolymer (2 to 10 mg) is placed in an alumina reaction cell (free volume of 0.227 cm^3), which is sealed with a cap assembly containing a disk of gold foil (25 µm thick) that contains a hole with a specific diameter (2.5 µm to 50 µm) through its center. The reaction cell is heated in a controlled manner, using the thermocouple to measure and control the temperature of the cell. As the reaction cell is heated, vapor from the sample, and any other compounds within the cell, fills the free volume. The vapor flows through the orifice and each constituent is identified and its rate of flow through the orifice is determined. The measurements provide the time-dependent rate of formation of each gaseous species that is present solely in the gas phase within the reaction cell. The measurements also provide the vapor pressure of gaseous species that are in quasi-equilibrium with material in condensed phases.

The pressure of gases within the reaction cell is controlled by the diameter of the orifice and the experimental conditions. The gas pressure within the cell is determined by a steady-state balance between the rate of gas formation from the sample and the rate of exhaust through the orifice. Smaller orifices will produce higher pressures for a given gas formation rate from the sample. For compounds in a two-phase quasi-equilibrium the pressure is determined by the temperature of the reaction cell and the properties of the compounds. In this case, a smaller orifice results in less of the gas exiting the reaction cell.

The data used to characterize the thermal decomposition processes are the identities and rates of formation of the different vapors that flow through the orifice and out of the reaction cell over a range of experimental conditions. The reaction conditions are controlled by altering the sample size, temperature, heating rate, orifice diameter and volume of the reaction cell.

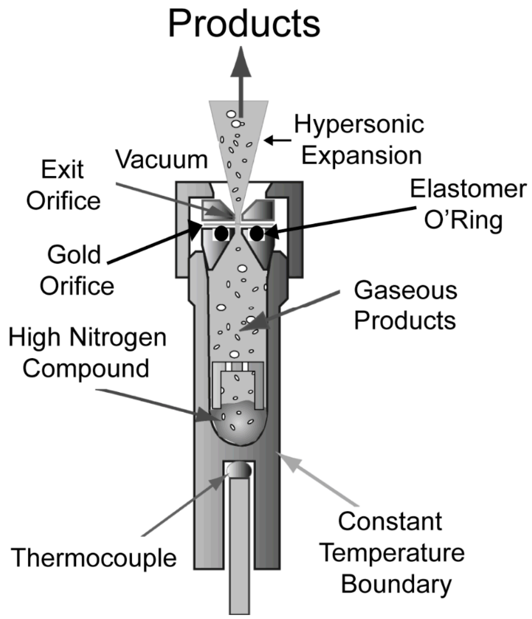


Figure 1. Cross section of a reaction cell illustrating the main features of an STMBMS experiment.

The FTICR Instrument

The Fourier-Transform ion-cyclotron-resonance mass spectrometer is a high mass resolution ($m/\Delta m$ > 100,000) and mass accuracy (< 1 ppm) ion-trap based mass spectrometer. The high mass accuracy of this instrument allows unambiguous determination of the empirical formula for each *m/z* value in a given spectra. Operation of this instrument, under conditions similar to the STMBMS instrument, allows chemical analysis results from the FTICR to be matched to the STMBMS data. This provides identification of the various gases that evolve from the reaction cell during an STMBMS experiment.

A basic chemical analysis thermal decomposition experiment using the FTICR mass spectrometer is straightforward. A 1.9 mm ID X 9 mm H quartz tube (internal volume: 0.026 cm^3) is loaded with ca. 1 mg of material and the open end of the tube can be either left open or 'necked-down' with a methane-oxygen minitorch to produce an exit aperture as small as 5μm in diameter. The resulting reaction tube is mounted in the heated tip of a direct-insertion probe (DIP) whose temperature can be varied in a controlled manner. The DIP probe is inserted into the FTICR mass spectrometer with the tip of the probe mounting into an electron-bombardment ionization (EI) source. Neutral gaseous species exiting the quartz reactor are ionized with 70eV electrons in the EI source and extracted into the FTICR for analysis.

RESULTS AND DISCUSSION

Thermal decomposition experiments have been conducted on unmodified and end-modified PGN prepolymer (~4000 Da). Experiments used two different heating rates (2.5 and 10°C/min) to separate the sequentially correlated reaction pathways, and three different reaction cell exit orifices (1000, 25, and 10μm) to separate direct, single-phase reactions from more complex, multi-phase reactions. Table I shows the experiments conducted on each sample and the conditions for each experiment.

Table I. STMBMS experiments conducted on unmodified and end-modified PGN prepolymer.

Sample	**Orifice (μm)**	**Heating Rate (°C/min)**	**Max Temperature (°C)**	**Sample Mass (mg)**
Unmodified	1000	2.5	450	2.47
	1000	10	300	1.73
	25	10	300	1.61
	10	2.5	300	1.82
Modified	1000	2.5	450	2.16
	1000	10	300	2.28
	25	10	300	1.57
	10	2.5	300	1.60

Table II shows the major *m/z* ion masses and corresponding empirical formulas for the gaseous species evolved from the PGN prepolymers. Column 1 gives the nominal (integer) *m/z* ion masses evolved in the STMBMS experiments. Column 2 and 3 show the fraction that each ion mass contributes to the total evolved signal for the unmodified and modified prepolymer, respectively. Column 4 shows the measured *m/z* values from the FTICR experiments and the corresponding empirical formula assignments for these exact masses is shown in column 5. Internal calibration of the FTICR spectra using PFTBA yielded sub-ppm (<1ppm) mass assignment error for the identified empirical formulas.

Identification of the decomposition products formed within the reaction cell is determined from the mass spectrometry data. The gaseous products that evolve from the reaction cell are ionized in the mass spectrometer. Ionization of the various decomposition products results in a mass spectrum consisting of a set of ion signals at various m/z values. A lower electron energy of ~20 eV is used to create ions from the decomposition products in the STMBMS instrument. This lower electron energy reduces fragmentation of the molecular ion (i.e., the ion formed by removal of an electron from the decomposition product) into daughter ions and makes interpretation of the mass spectral data somewhat simpler. To determine which ion signals originate from the same decomposition product, a cross-correlation analysis of the data from the mass spectra recorded during the course of an experiment is used to divide the ion signals at various m/z values into temporally correlated groups. The stoichiometry of the ions in each group, as determined by FTICR measurements, is used to identify the decomposition products formed within the reaction cell. Once identified, one ion signal is selected from each group to represent the temporal behavior of the rate of formation of each decomposition product formed within the reaction cell. Comparison of these representative ion signals with the mass loss data, collected in the STMBMS experiments, allows assessment of the relative rate of formation of the various products during thermal decomposition of a sample. The temporal behaviors of the representative ion signals provide insight into the sequence of events in the reaction process that control the thermal decomposition of the sample within the reaction cell.

Table II. Major species evolving from PGN prepolymer.

m/z_value	**%_Signal unmodified**[a]	**%_Signal modified**	**Exact Mass**	**Empirical Formula**
30	19.86	19.84	29.9975	NO
			30.01	CH_2O
			30.0338	CH_4N
18	9.15	5.74	N/A	H_2O
57	7.01	7.49	57.0335	C_3H_5O
29	6.79	7.33	29.0022	CHO
			29.0386	C_2H_5
103	5.69	6.01	103.039	$C_4H_7O_3$
44	4.35	5.88	43.9893	CO_2
			44.0005	N_2O
			44.0131	CH_2NO
			44.0257	C_2H_4O
46	4.24	2.80	45.9924	NO_2
			46.0288	CH_4NO
61	3.96	5.06	61.0284	$C_2H_5O_2$
73	3.64	3.71	73.0284	$C_3H_5O_2$
116	3.26	2.25	116.0341	$C_4H_6NO_3$
28	3.18	3.93	27.9943	CO
			28.0056	N_2
			28.0182	CH_2N
			28.0308	C_2H_4
87	3.17	3.49	87.0441	$C_4H_7O_2$
31	2.72	2.95	31.0179	CH_3O
43	2.55	2.82	43.0179	C_2H_3O
71	2.49	2.31	71.0492	C_4H_7O
86	2.38	2.04	86.0363	$C_4H_6O_2$
58	2.23	2.32	58.0413	C_3H_6O
55	1.81	1.89	55.0542	C_4H_7
45	1.72	1.85	45.0335	CH_3NO
117	1.69	1.75	117.0548	$C_5H_9O_3$
101	1.63	1.71	101.0598	$C_5H_9O_2$
131	1.61	1.99	131.0341	$C_5H_7O_4$
56	0.88	1.04	56.0257	C_3H_4O
42	0.72	0.80	42.01	C_2HOH
27	0.63	0.91	27.0104	HCN

[a] *m/z* list sorted by decreasing %Signal of unmodified prepolymer

Figure 2 shows the thermogravimetric (TGA) data from the 25μm thermal decomposition experiments for the PGN prepolymers. The unmodified PGN prepolymer data is shown in the upper frame, the OH end-modified in the lower frame. Both prepolymers show similar TGA features. The mass loss for each prepolymer indicates a decomposition that occurs over a broad temperature range (~100-300°C) and shows three distinct thermal features: (1) a slow, early process (100-195°C) accounting for ~5% of the overall mass loss, (2) a fast process (195-215°C) accounting for ~80% of the mass loss, and (3) a slow, late process (215-300°C) accounting for ~15% of the remaining PGN mass and generating the final non-volatile residue (~3% of the total mass).

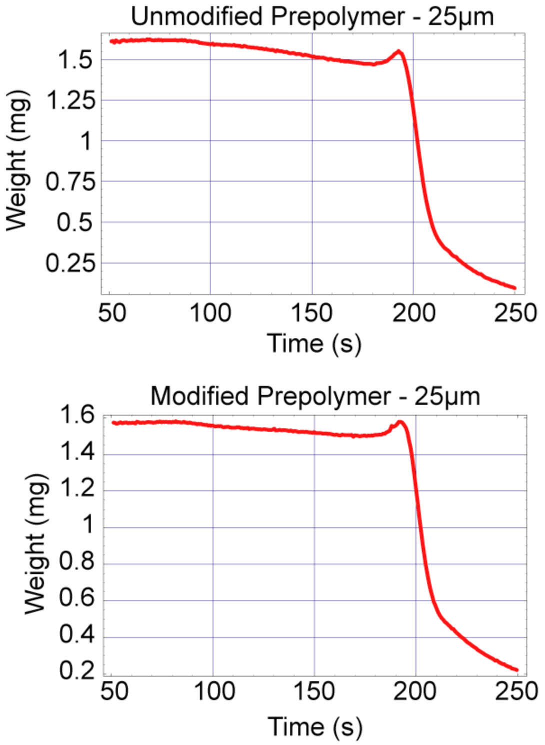


Figure 2. Thermogravimetric data for the STMBMS thermal decomposition of unmodified and OH end-modified PGN prepolymer.

Figure 3 shows the ion signals for the four reaction pathways controlling the decomposition of the PGN prepolymers. The unmodified prepolymer is shown on the left, the modified prepolymer on the right. The first pathway for the unmodified PGN (A) corresponds to early elimination/decomposition of the CH_2-O-NO_2 functional moiety to form principally CH_2O, NO_2, and NO, and leaves a highly reactive backbone from the nitrate ester elimination. Pathway two (B) corresponds to reactions of early products with the reactive backbone from pathway one to form HCN and water. Pathway three (C) corresponds to a second reaction of early products with the reactive backbone to form CO and CO_2/N_2O. The lower frame (D) shows pathway four, and corresponds to decomposition/reaction of the remaining degraded backbone to form the final non-volatile residue (NVR). The OH end-modified prepolymer data shown on the right of Figure 3 shows the same set of four reaction pathways that controls the unmodified prepolymer decomposition. The initial formation of NO_2 appears earlier in the unmodified prepolymer, this could be attributed to elimination of the terminal NO_2, which is not present in the OH end-modified prepolymer. This early elimination has no apparent effect on the rest of the decomposition, as indicated by the similar features of panels B-D in both the unmodified and end-modified prepolymer. The OH end-modification has not altered the overall decomposition chemistry for the uncured PGN prepolymer.

The two fast reaction pathways, 2 and 3, shown in Figure 3, correspond to the rapid mass loss indicated in Figure 2. The rapid mass loss accounts for ~80% of the starting PGN mass. This large mass loss for pathway 2 and 3 indicates these pathways must involve reactions of the reactive backbone and early gas products, as the nitrate ester groups account for only ~60% of the PGN prepolymer mass. The slowly decreasing 'tails' in pathway 3 and 4 correspond to the slow, late mass loss region shown in Figure 2. This final mass loss region represents <15% of the overall mass loss and accounts for the formation of a viscous, thermally stable (up to 300°C), non-volatile residue.

As presented above, the STMBMS data provides support for a thermal decomposition mechanism involving four reaction pathways. Figure 4 shows the four reaction pathways developed from the STMBMS and FTICR data. The first reaction shown in Figure 4 is a simple elimination reaction of the CH_2-O-NO_2 functional moiety from both the backbone and the terminal end of the prepolymer and a concerted scissioning reaction of the O-NO_2 nitrate ester group to form CH_2O, NO_2, leaving a backbone containing multiple reactive radical sites. NO is also formed in the first pathway by oxidation of the backbone by NO_2. The backbone remains open to further attack at the radical sites remaining from the elimination reaction. Pathways 2 and 3 in the decomposition process are a set of fast reactions involving interaction of the NO from pathway 1 with the reactive backbone. In pathway 2, the reaction forms principally HCN and water, while in pathway 3, the reaction forms CO and CO_2/N_2O. Pathway 3 separates from pathway 2 by its slower rate of decrease and significantly longer 'tail'. The final reaction is the reaction of the remaining backbone with CO_2 from pathway three to form the final non-volatile residue through formation of a polymeric carbonyl rearrangement of the reactive backbone.

Chen and Brill[2] studied the thermal decomposition of nitrocellulose (NC), poly glycidyl nitrate (PGN), poly vinyl nitrate (PVN), and poly nitratomethylmethyloxetane (NMMO) by their simultaneous mass and temperature change (SMATCH)/FTIR spectroscopy technique. Their results show the dominant gas products liberated from the decomposition of these nitrate esters was NO, CO, and CO_2, with lesser amounts of NO_2. The PGN showed substantial CH_2O and larger amounts of NO_2. The increased NO_2 was attributed to the liquid state of the PGN prepolymer allowing the liberated NO_2 to reach the gas-phase with less interaction with the prepolymer backbone than with the cured NC, PVN and NMMO, where the NO_2 must migrate through the polymer matrix before release into the gas-phase. This also accounts for the lesser amount of NO formed as a result of reduction of NO_2 by interaction with the polymer backbone. CH_2-O-NO_2 homolysis, to form formaldehyde (CH_2O) and NO_2 was seen as the dominant initial step in the decomposition of these nitrate esters. Formation of the viscous residue at the end of the decomposition was attributed to reactions of the reactive backbone that was formed after the initial CH_2-O-NO_2 elimination. The first reaction pathway shown in Figure 4 (1) accounts for the CH_2-O-NO_2 elimination, subsequent cleavage to CH_2O and NO_2 and a lesser amount of NO from oxidation of the reactive backbone with the NO_2, along with formation of a reactive backbone containing multiple radical sites from the elimination reaction.

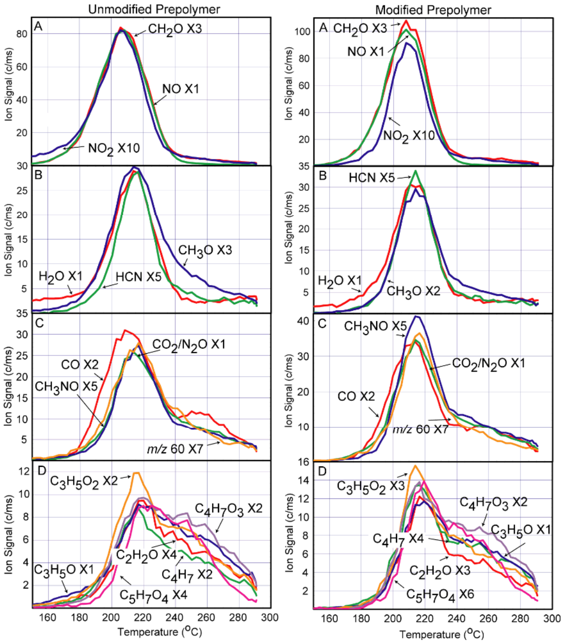


Figure 3. Ion signals from the four reaction pathways controlling the decomposition of the PGN prepolymer. The unmodified PGN is shown on the left, the modified PGN on the right.

Pathway 3 in Figure 4 is consistent with Chen and Brill's[2] measurements of the gas-phase evolution of CO and CO_2, which they attributed to extensive condensed-phase reactions occurring between the early gas products and the reactive backbone before release of the resulting gas products.

Ling and Wight[4] investigated the formation of the polymeric non-volatile residue from PGN prepolymer. Their work concluded that this was a polymerization reaction occurring at the open radical sites along the PGN backbone and resulting in formation of a polymeric residue with carbonyl functionality. Pathway 4 (4) in the proposed reaction mechanism of Figure 4 is the same carbonyl formation reaction, occurring along the entire backbone to form the final non-volatile residue recovered in the STMBMS experiments.

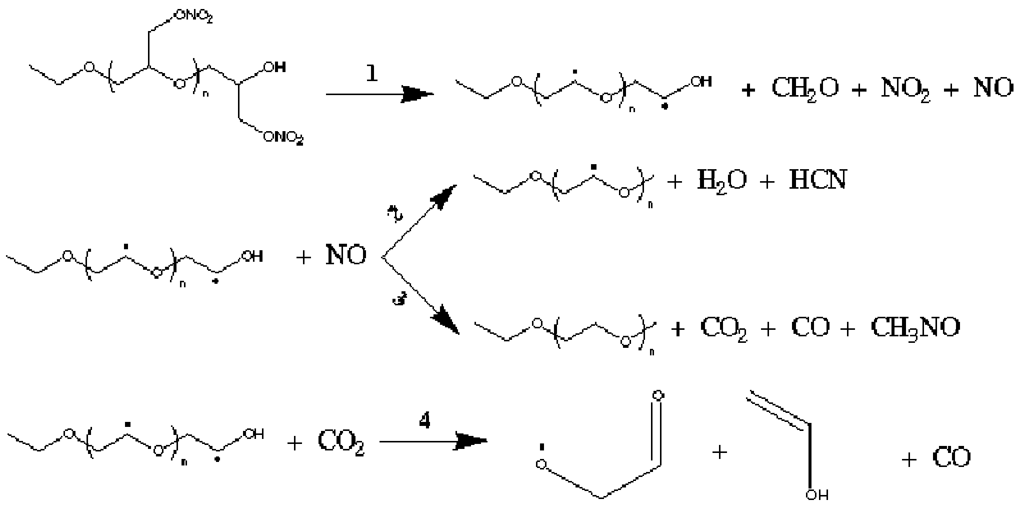


Figure 4. Reaction mechanism controlling the thermal decomposition of PGN prepolymer.

SUMMARY AND CONCLUSIONS

STMBMS and FTICR thermal decomposition experiments on uncured PGN prepolymer provide insight into the dominant reaction mechanisms controlling the decomposition behavior. Unmodified and OH end-modified PGN prepolymer have been studied to understand the effect that chemical modification of the prepolymer end-groups has on the thermal decomposition process.

The decomposition of the unmodified PGN prepolymer proceeds through a process involving four reaction pathways: (1) elimination of CH_2O and NO_2 and corresponding formation of NO, two fast reactions of NO with the reactive backbone remaining from pathway one to form (2) H_2O and HCN and (3) CO and CO_2/N_2O, and (4) the decomposition of the remaining reactive backbone to form a non-volatile residue.

Chemical modification of the terminal end of the prepolymer by replacing the terminal nitrate ester (O-NO_2) by OH has no effect on the overall decomposition process. This is consistent with the dominant reactions being elimination of the CH_2-O-NO_2 nitrate ester functional group and subsequent reactions of the gas products with the remaining backbone.

The gas-phase products evolved from the condensed-phase thermal decomposition process form the reactant ‘pool’ for the combustion reactions of the cured PGN rubber. Any substantial alteration of the decomposition process could affect either the combustion mechanism, through a change in the distribution of the evolved products, or the combustion kinetics, through a change in the evolution rates of the gaseous products. The reaction mechanism developed from this investigation indicates that the decomposition process is not affected by the OH end-modification. Based on these results, it would not be expected that the OH end-modification would affect the combustion kinetics of the resulting, cured PGN rubber.

FUTURE WORK

Future work will focus on elucidating the processes that control the decomposition of the cured PGN polymer (rubber) and the effect different diisocyanate curatives have on the decomposition chemistry.

ACKNOWLEDGEMENTS

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