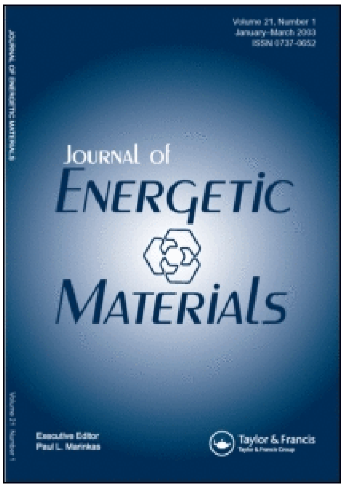

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Deuterium Effect on Thermal Decomposition of Deuterated Gap: 1. Slow Thermal Analysis with a TGA-DTA-FTIR-MS

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The knowledge of the degradation mechanisms of propellants is a key factor in understanding some performance issues of chemical propulsion systems. The thermal decomposition of GAP and a deuterated analog was studied. Thermogravimetric analyses coupled to differential thermal analysis, Fourier transform infrared spectrometry, and mass spectrometry were employed to evaluate

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the complete decomposition profile of GAPs. Evidence of labeled gaseous compounds were found both in mass spectra and in the FTIR spectra, where new frequencies associated with isotopic labeled gaseous products were detected. An imine-bearing species was detected among the decomposition products, apparently originating from the breakdown of the azide group.

Keywords: decomposition, GAP, isotope effect, thermal

Introduction

A knowledge of decomposition mechanisms of fuel-rich propellants or gas generators, as much in terms of the nature of their decomposition products as for the rate at which smaller species are produced, is a key factor in understanding performance issues in chemical propulsion systems. Several workers have studied the thermal decomposition and combustion of glycidyl azide polymer (GAP), an energetic binder that was first developed as a novel ingredient for the most recent generation of solid rocket propellants. The thermal decomposition of this kind of polymer was studied using techniques such as SMATCH/FTIR [1], rapid thermolysis and IR [2], T-jump/FTIR [3], thermal analysis [4,5], mass spectrometry [6],and burning rate evaluation [7]. However, GAP has also become a serious candidate as the main ingredient of future ramjet fuel formulations because of its chemical stability and its appropriate burn rate exponent. The simplified structure of the GAP monomer is shown in Fig. 1a. Despite recent progress in experimental work aimed at identifying the key steps of GAP decomposition, its detailed mechanism remains partially unproven or poorly understood. The generally accepted first step of this decomposition reaction is the cleavage of the azide group ($-N_3$) on the GAP monomer. While two possible routes for the initial breakdown of the $-N_3$ have been suggested, no consensus exists about the most probable one, and the lack of experimental evidence makes it difficult to determine. According to Kubota [7] and Jones [8,9], the first step in the decomposition

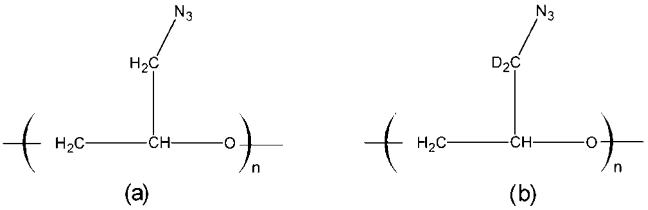

Figure 1. Structures of the monomer of a) GAP, and b) d-GAP.

of GAP is a simultaneous liberation of molecular nitrogen and hydrogen. An alternative path suggests the initial formation of HCN, and then CO, CH_2O, NH_3, and other hydrocarbons. Recently, Fazhoglu and Hacaloglu [10] have studied the thermal decomposition of GAP by direct insertion probe mass spectrometry. They proposed the few reaction steps shown in Fig. 2 to explain the thermal degradation of GAP. Small molecules are the main species detected and are the result of the complete cleavage of GAP backbone. This research uses a different approach for studying the thermal decomposition of GAP, an approach that could be extended to other azido-polymers. By using deuterated monomers in the synthesis of GAP, one obtains a polymer that, in thermal decomposition studies, will produce labeled combustion products. More specifically, if some of the hydrogen atoms of the monomer are replaced by deuterium, these deuterated portions of the original molecules can be traced back among the decomposition products. By carefully selecting the deuterated sites on the monomer, several ratios among stable decomposition species can be obtained and the controlling steps of the reaction mechanism can be identified. The structures of GAP repeat units studied are shown in Figures 1a and b.

In this work, we attempt to correlate the primary steps of GAP decomposition with its molecular structure by systematically relating the detected species to macroscopic thermal properties of one type of d-GAP. This article reports on the first part of this study devoted to the slow pyrolysis of a normal

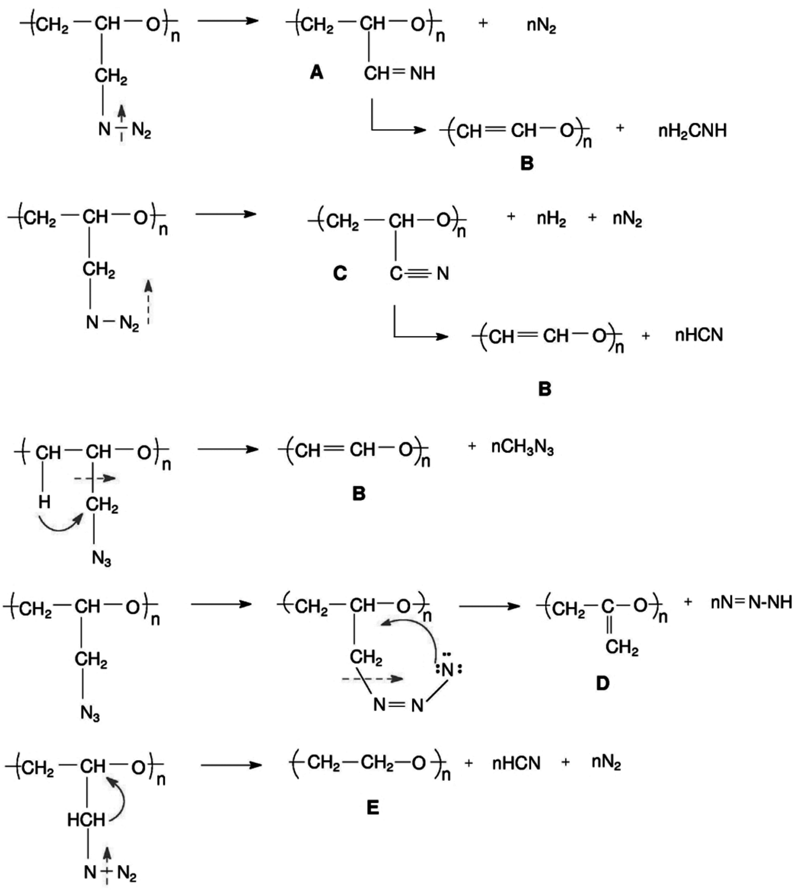

Figure 2. Proposed pathways for azide group abstraction on the GAP monomer [10].

GAP and a deuterated GAP by observing the decomposition process in detail with a powerful analytical tool, a TGA-DTA-FTIR-MS. Later, the kinetic deuterium isotope effect on the thermal decomposition will be investigated and, finally, the pressure effect on the pyrolysis of the GAPs using a high-pressure/high-temperature cell FTIR and gas chromatography will also be reported.

Experimental

GAP and its corresponding deuterated analog were obtained from the successive polymerization of epichlorohydrin (ECH) and azidation of the resulting polymer upon a procedure previously described by Ringuette et al. [11]. Thermal characterization of a normal and a deuterated sample of GAP was conducted using TG-DTA-FTIR-MS in duplicate. A simultaneous TG-DTA 2960 module was used to measure mass changes (TG) and the temperature difference between the sample and a reference material (DTA). A Bomem MB100 Fourier transform infrared spectrometer (FTIR) and a Balzers Thermostar GSD300 quadrupole mass spectrometer (MS) were used to analyze the evolved gas. Figure 3 illustrates the experimental setup. Approximately 5 mg of sample and reference were placed in alumina pans, and the DTA reference material used was platinum. The sample and the reference were heated from 30 to 650°C at a rate of 10 K/min. The experiments were performed in 100 mL/min stream of helium. The samples were purged with a helium flow of ~180 mL/min for 30 min prior to the heating profile. TG mass, DTA baseline, and temperature [12] calibrations (indium, aluminum, and gold) were performed prior to the experiments. The FTIR interface consisted of a 5-mm i.d.

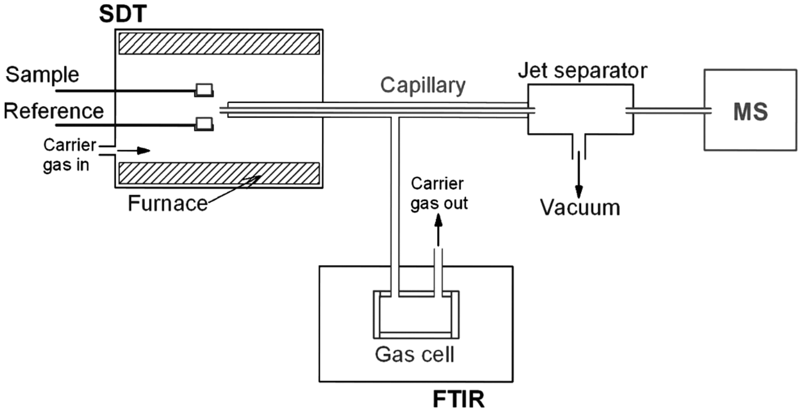

Figure 3. TGA-DTA-FTIR-MS experimental setup.

Teflon tube and a 10-cm Pyrex cell with a 50-mL volume and KBr windows. A quartz microfiber filter was placed at the FTIR inlet. The acquisition rate of the FTIR was two scans per minute and the sample travel from the TG-DTA furnace outlet to the FTIR was estimated at $\sim$10 s. Scanning frequencies ranged from 500 to 5000 cm^{-1}. For the MS, the heated quartz capillary interface was placed near the sample pan in the TG-DTA furnace. Data were gathered using the Balzers Quadstar 422 software, programmed to acquire data using a bargraph scan from 5 to 100 amu (atomic mass unit) at a speed of 0.2 s/amu.

Results and Discussion

This article reports the slow pyrolysis of a normal and a deuterated GAP using a TG-DTA-FTIR-MS apparatus to monitor the formation of combustion products during the decomposition process. The complete set of data for these analyses is shown in Figs. 4 and 5. The sample mass and the temperature difference (ΔT) were plotted against temperature in Figs. 4a and 5a. The absorbance (A) versus temperature for the evolved gases detected by FTIR is shown in Figs. 4b and 5b. The MS data are presented as ion current versus temperature for the selected mass fragments (Figs. 4c and 5c). The summary of experiments results is presented in Table 1.

The mass spectrometry analyses of samples submitted to the pyrolysis process showed that the main thermal decomposition of GAP and d-GAP occurred in the temperature range of 220–300°C. The peaks due to low-mass fragments ($m/z < 50$ amu) were very abundant and no high-mass fragments were found in the range of 5–100 amu used. The complete dissociation of the polymer backbone was not observed since a residue of about 20% (mass) is found at the end of experiment. For both polymers studied, the base peak at 28 amu was the most prominent one, clearly due to molecular N_2, indicating that the azide rupture reaction was the main step of thermal decomposition, as proposed in the literature.

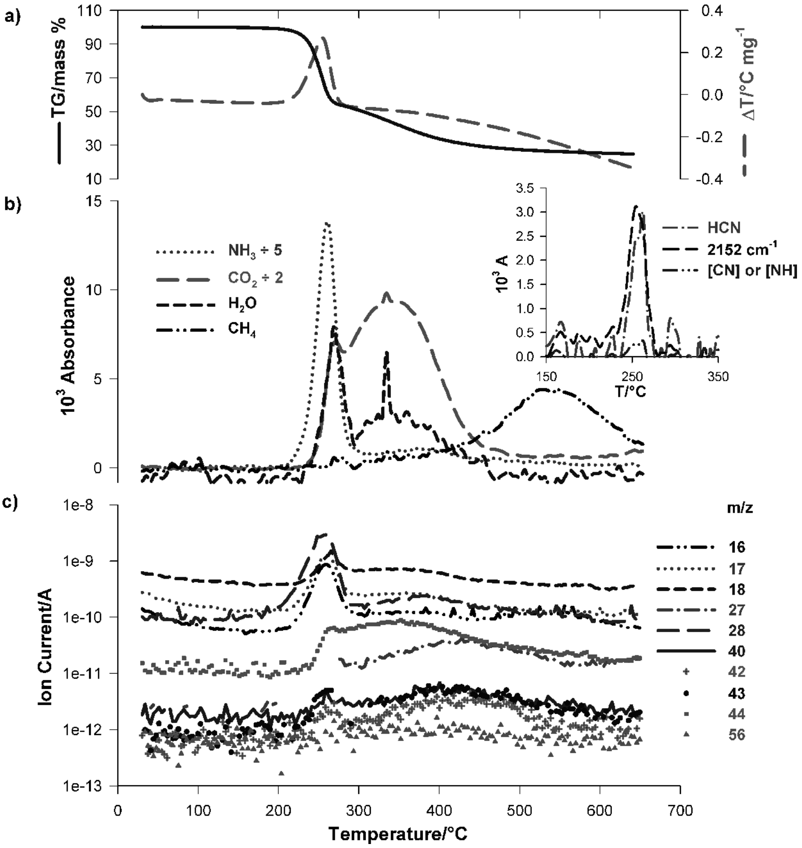

Figure 4. a) TGA-DTA, b) FTIR, c) MS results for 5 mg of GAP (10 K/min).

The significant and detectable differences between normal and labeled GAPs are the evolution of m/z 19 and 20 from d-GAP. As compared in Fig. 6, the evolution of m/z 19 started at ~250°C and was observed during d-GAP decomposition, but not for GAP. Above ~250°C, the evolution of m/z 20 was also slightly higher in d-GAP than in GAP. This distinction between the two polymers suggests that a new compound, probably labeled, was formed in the decomposition process of

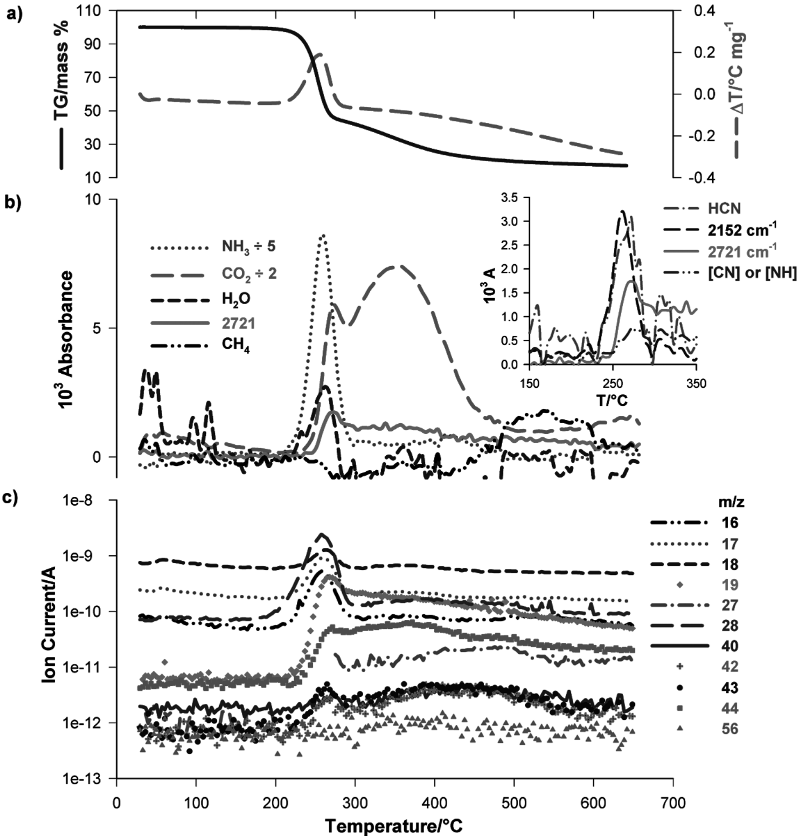

Figure 5. a) TGA-DTA, b) FTIR, c) MS results for 5 mg of d-GAP (10 K/min).

the deuterated GAP. Table 2 gives the proposed assignments for the major fragments in each mass spectrum.

Figures 4a and 5a depict the thermograms of the GAPs. The thermal decomposition patterns are similar for the two energetic polymers, except that the first weight loss was higher (56 ± 1%) in the d-GAP than for the normal GAP (48 ± 1%). These results are comparable with the thermal analysis obtained in a previous study in similar conditions [11].

Table 1
Summary of TG-DTA-FTIR-MS results

Sample	GAP	d-GAP
Mass/mg	5.4 ± 0.4	5.3 ± 0.1
Onset temperature/°C	185 ± 1	188 ± 2
1st mass loss %	48 ± 1	56 ± 1
Peak area/$_1$°C min mg^{-}	1.05 ± 0.06	0.86 ± 0.04
2nd mass loss %	30 ± 1	26 ± 1
FTIR results	NH_3, CO_2, H_2O, HCN, CH_4, 2152, 2282 ([CN] or [NH]) cm^{-1}	NH_3, CO_2, H_2O, HCN, CH_4, 2152, 2282 ([CN] or [NH]) 2721 cm^{-1}
10^3 [NH_3]/A mg^{-1}	63 ± 8	46 ± 4
10^3 [NH_3]/A mg^{-1}	18 ± 0.4	15 ± 1
10^3 [NH_3]/A mg^{-1}	7 ± 2	5 ± 2
MS results	m/e 12, 13, 14, 15, 16, 17, 18, 25, 26, 27, 28, 29, 30, 32, 38, 39, 40, 41, 42, 43, 44, 45, 46, 50, 51, 52, 53, 54, 55, 56, 69	m/e 12, 13, 14, 15, 16, 17, 18, **19**, **20**, 25, 26, 27, 28, 29, 30, 32, 38, 39, 40, 41, 42, 43, 44, 45, 46, 50, 51, 52, 53, 54, 55, 56, 69

The evolution of each mass peak was tracked according to its corresponding and known absorbance frequencies in FTIR. The FTIR spectra are given in Figs. 4b and 5b. Accordingly, CO_2 (m/z = 44), N_2 (m/z = 28), CO (m/z = 28), CH_4 (m/z = 16, and 15), NH_3 (m/z = 17, 16, and 15), H_2O (m/z = 18), and HCN (m/z = 27 and 26) are identified for each polymer. However, for HCN, the absorbance band at 712 cm^{-1} that followed the temperature evolution was found to be weak and partially hidden in noise.

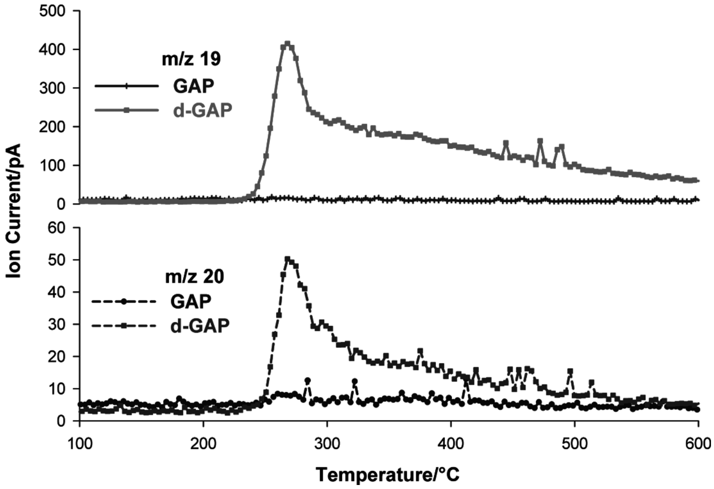

Figure 6. Mass evolution a) m/z = 19 and b) m/z = 20 from GAP and d-GAP (heating rate 10 K/min).

FTIR spectra of gaseous products from the deuterated GAP degradation showed the presence of a new band at $2721\,\mathrm{cm}^{-1}$. Figure 7 illustrates the evolution of this IR band with temperature for a few unidentified m/z peaks (m/z = 19, 20, and 30). It can be seen that the FTIR profile has the same aspect of m/z 30, 20, and 19. For the GAP decomposition, this profile was not obtained. A possible explanation to this fact is the imine formation in Fig. 2, structure **A**. This structure gives the fragmentation peak of CH = NH (m/z = 28). In the non deuterated GAP, the fragment at m/z 28 is not distinguished from N_2 and CO evolution, but this imine could be associated with absorbance peaks at 3332 and $1652\,\mathrm{cm}^{-1}$ present in the FTIR spectra [10,11,13]. In the labeled compound, we have selectively substituted deuterium atoms close to the azide group (Fig. 1) to identify the chemical rearrangement after the N_2 rupture in the thermal reaction. Consequently, if the deuterated imine is formed (CD = ND, m/z = 30), a possible mass evolution should be detected and a specific absorbance peak too. It seems to be the case in the decomposition of d-GAP.

Table 2
Mass spectra assignments of GAP and d-GAP during thermal decomposition

m/z	GAP assignment	d-GAP assignment
12	C	C
13	CH	CH
14	CH_2, N	CH_2, CD, N
15	CH_3, NH	CH_3, NH
16	O, CH_4, NH_2	O, CH_4, NH_2, CD_2, ND
17	NH_3, OH	NH_3, OH
18	H_2O	H_2O, ND_2, OD
19		**HDO, ND_2H, CHD_3**
20		**ND_3, D_2O, CD_4**
25	HCC	HCC
26	C_2H_2, CN	C_2H_2, CN, DCC
27	HCN	HCN
28	N_2, CO, C_2H_4, CH=NH	N_2, CO, C_2H_4, DCN
29	HCO, CH_2NH	HCO, CH_2NH CH=NH or CH=ND
30	H_2CO	H_2CO, CH=ND
32	O_2	O_2
38	CCN	CCN
39	CHCN	CHCN
40	CH_2CN	CH_2CN, CDCN
41	CH_3CN	CH_3CN
42	CH=CHO	CH=CHO
43	C_2H_3O, HN_3	C_2H_3O, HN_3, CD_2HCN
44	CH_2CH_2O, CO_2	CH_2CH_2O, CO_2
56	CH_2N_3, C_4H_8, C_3H_4O	CH_2N_3, C_4H_8, C_3H_4O
99	GAP monomer	

The proposed mechanism [10] in Fig. 2 does not explain the formation of ammonia. However, this product is easily observed in the decomposition pattern in Figs. 4 and 5 as a major gaseous compound. Once again, if the selectively labelled GAP leads to imine, and that imine leads to the formation of partially

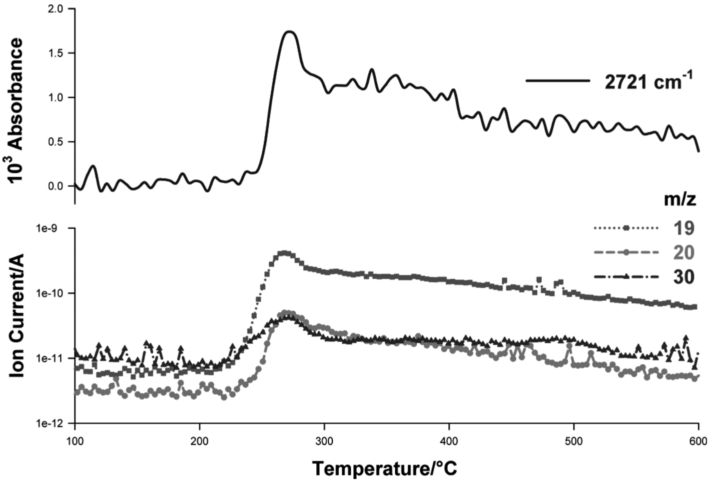

Figure 7. Temperature evolution of 2721 cm^{-1} in d-GAP decomposition.

deuterated ammonia with a proton migration, the m/z 19 could be explained by:

$$\mathrm{RH - CD = ND \rightarrow ND_2H + other\ products} \qquad (1)$$

Conclusions

This paper presents an experimental investigation on the thermochemical decomposition processes of glycidyl azide polymers obtained from deuterated epichlorohydrin. These isotopic-labeled polymers were found to be useful to pursue further studies aimed at identifying the key steps in the GAP thermal decomposition process. Using techniques such as TGA-DTA-FTIR-MS, a more complete source of information and better insights about the mechanisms involved in the thermal decomposition of GAP and its selectively deuterated derivative could be obtained.

The comparison between the slow thermal decomposition of these GAPs showed a very similar profile. The only significant and detectable differences were the evolution of m/z 19 and 20 from deuterated GAP. The presence of a new infrared absorbance in the decomposition products of the labeled polymer was also observed. The detection of gaseous labelled compounds, possibly imines, confirms the decomposition pathway recently proposed by Fazhoglu [10]. N_2 is the first step of decomposition, followed by a H-migration to produce an intermediary chemical species, the imine. This compound is then broken to form low-mass final products including HCN, NH_3, CO, CO_2 and methane as confirmed by mass spectrometry.

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